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DEPARTMENT OF COMMERCE

TECHNOLOGIC PAPERS

OF THE

BUREAU OF STANDARDS

S. W. STRATTON, DIRECTOR

No. 144

PROPERTIES OF AMERICAN BOND CLAYS AND THEIR USE IN GRAPHITE CRUCIBLES AND GLASS POTS

BY

A. V. BLEININGER, Ceramic Chemist

Bureau of Standards

ISSUED JANUARY 28, 1920



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PROPERTIES OF AMERICAN BOND CLAYS AND THEIR USE IN GRAPHITE CRUCIBLES AND GLASS POTS

By A. V. Bleininger

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Part I—PROPERTIES OF AMERICAN BOND CLAYS

I. INTRODUCTION

Considerable activity has prevailed during the last three years in searching for domestic refractory clays possessing sufficient plasticity, bonding power, and strength to be used in the manufacture of glass refractories, graphite crucibles, and similar products. The properties of the European clays formerly imported

for this purpose have been described in a previous publication.¹ The clay-products section of the Bureau of Standards, during the last two years, has come into possession of a number of samples of American plastic bond clays. It was thought advisable to publish the results of tests made upon clays of this type. The tests made consisted in the determination of the water of plasticity, the drying shrinkage (by volume), the apparent specific gravity in the dried state, the rate of slaking, the modulus of rupture of dried bars made from each clay with and without admixture of sand, the porosity and volume changes at different firing temperatures, and the softening points compared with those of the standard pyrometric cones. From the water content and the drying shrinkage the ratio of pore water to shrinkage water was computed, as well as the percentage of shrinkage water in terms of the true clay volume and the total water content.

II. METHODS OF TESTING

1. *Water of Plasticity.*—The entire sample was first ground and screened through a 12-mesh sieve, thoroughly mixed, and a sufficiently large portion removed for all the tests. The clay was made up with water and thoroughly wedged till it had assumed what was considered the best plastic condition. It was then made up into briquets 2 by 1¼ by 1 inches and into bars 1 by 1 by 7 inches. The weight of several briquets was determined in the wet state and after complete drying by heating to 110° C. The water of plasticity was taken to be the weight lost in drying, computed in per cent of the dry weight.

2. *Drying Shrinkage.*—In carrying out this determination the volume of the briquets was found by immersing them in kerosene immediately after molding and, after standing for some hours, determining their volume in a volumometer of the Seger type, provided with a burette, reading to 0.05 cc. After removing the specimens they were allowed to dry, first, at atmospheric temperature and then at 110° C. The dry specimens were weighed at once, again immersed in kerosene, usually for 12 hours or longer, and the volumes were determined as before. From the differences in the volumes of the briquets in the wet and in the dry state the shrinkage was computed in terms of the dry volume. From the weights of the dry specimens and their volumes the apparent specific gravity was readily computed by dividing the volume, expressed in cubic centimeters, into the weight, in grams.

¹ Bureau of Standards Tech. Paper No. 79.

From the wet and dry weights and the wet and dry volumes of the briquets and the true specific gravity of the clay it was possible to calculate the volume of the shrinkage and the pore water in terms of the true-clay volume. These computations were based on the following obvious relations:

$$\frac{100s(W_1 - W_2)}{W_2} = a = \text{volume of total water, in terms of the}$$

true-clay volume, expressed in per cent, and

$$\frac{100s(v_1 - v_2)}{W_2} = b = \text{volume of shrinkage water, in terms of the}$$

true-clay volume, expressed in per cent.

In these formulas

s = specific gravity of clay, approaching the value 2.60 quite closely for all clays of this type.

W_1 = weight of briquet in the wet state.

W_2 = weight of dry briquet.

v_1 = volume of briquet in the wet state.

v_2 = volume of the briquet in the dry state.

The value $(a - b)$ represents, similarly, the volume of pore water and the ratio $\frac{(a - b)}{b}$ the relation of pore to shrinkage water. By

dividing b by a and multiplying by 100 the percentage of shrinkage water, in terms of the volume of total water, may be computed.

3. *Rate of Slaking*.—This was determined by making mixtures of the clays with potters' flint in the proportion of 1:1 and molding into $\frac{7}{8}$ -inch cubes, which were dried first at atmospheric temperature, and finally at 110° C. Upon immersing the cubes in water at room temperature, suspending them in coarse-mesh baskets, the time of slaking was observed. The more plastic the clay, the longer was it found to resist this action.

4. *Modulus of Rupture*.—The clays in the form of bars 7 by 1 by 1 inches were dried, then heated to 110° C, and upon cooling were broken transversely. From the dimensions of the pieces and the load required to fracture them the modulus of rupture was computed according to the usual formula. According to the quantity of clay available from 10 to 15 such bars were made and tested. Another series of such test specimens was prepared from the mixture of clay and sand in the proportion of 1:1. The sand corresponded to the following sieve analysis:

	Per cent
Residue on 40-mesh sieve.....	53.4
Residue on 60-mesh sieve.....	35.8
Residue on 80-mesh sieve.....	6.9
Through 80-mesh sieve.....	3.9

All of the sand passed a 30-mesh sieve.

The results given are the averages of at least 10 tests in each case.

5. *Burning Behavior of the Clays.*—The briquets, after thorough drying, were placed in a test kiln, fired with natural gas, and burned at a rate corresponding to a temperature increase of 20° C per hour above 800° C. At temperatures beginning with 1050° C briquets were drawn and cooled slowly by being put in a pot furnace brought to red heat or by being covered with hot sand. When cooled, these specimens were weighed, immersed in water, boiled under diminished pressure for five hours, weighed while suspended in water, and weighed in air while still fully saturated with water. From these data the porosity was calculated by the Purdy formula:

$$\frac{100 (w-d)}{(w-s)} = \text{per cent porosity,}$$

where

w = wet weight, in air, of briquet.

d = dry weight.

s = weight suspended in water.

The volumes of the briquets were determined by means of the volumenometer, using kerosene as the displacing liquid. The volume shrinkage or expansion was invariably expressed in terms of the original volume in the dried state.

Both the porosity-temperature and the volume-temperature relations are extremely significant in expressing the burning behavior of the clays. They show at what temperature the state of greatest density (vitrification) is reached, and they also indicate at what point overburning occurs due to the formation of vesicular structure. The volume relations are particularly useful in indicating any expansion which may occur due to the above cause or to the effect of the free quartz which may be present. In general, it may be said that the longer the temperature interval between the point of greatest density (lowest porosity) and the temperature of overburning, and likewise the higher the temperature at which overfiring occurs, the more useful should be the clay as a refractory material.

Clays which reach the state of maximum density only very gradually, owing to their high content of silica, and which never become really vitrified, are also a very useful type, provided they fulfill the other requirements of plastic bond clays. Such materials are particularly valuable for use in glass refractories. For

crucibles, gas-tight muffles, etc., the clays burning dense at a comparatively low temperature, but showing no evidence of overfiring up to quite a high temperature, should be most suitable.

III. RESULTS

The numerical results obtained in these tests are compiled in Tables 1 and 2. In analyzing the data thus presented it might be advisable to consider briefly the types of clay with which we are dealing here and to establish some arbitrary rules which might aid in classifying the materials. It should be realized that such a classification is necessarily of a tentative character. The clays must be considered from two standpoints, viz, their behavior in the raw state and in burning. From the first point of view two criteria might be employed, the transverse strength of the 1:1 clay-sand mixtures and the ratio of pore to shrinkage water. Arbitrarily we might, perhaps, say that clays showing a modulus of rupture of 325 pounds per square inch or more belong to class A and those between 225 and 325 pounds to class B. The ratio of pore to shrinkage water should in no case exceed 1 for clays of the A type. Further differentiation does not seem possible at the present time. For strong, heavy, plastic clays, low in free silica, the ratio undoubtedly should not exceed 0.75, but siliceous bond clays, such as the Grossalmerode, can not comply with this specification. It might be added that a certain degree of tolerance—say 5 per cent of the values involved—should be allowed in differentiating clays as regards their mechanical strength and the porosity-shrinkage ratio.

With reference to the burning behavior, the overfiring temperature and the softening point are the principal criteria. For very severe service clays of this type should not become decidedly vesicular at a temperature below 1425° C, and should not show a softening point below that of cone 31. It is realized that this specification is not fair to certain plastic clays which are valuable for use in connection with graphite crucibles, especially for brass melting. It seems, however, that even for this purpose the overfiring temperature should not be much below 1400° C and the softening temperature not below that of cone 30. Materials below either of these requirements should not be considered as being high-grade bond clays. Attention might be called to the fact that more weight should be placed on the overfiring temperature than on the softening point. Other conditions being satisfactory, failure of a clay to comply with this requirement within one cone should

not result in its rejection. It is also necessary to note carefully the degree or the rate of overfiring. It is evident that small or gradual changes are not necessarily of importance with reference to the deterioration of the material.

Concerning the general burning behavior of the clays, several classes are to be distinguished in regard to the temperature at which they become dense and that at which overfiring takes place. In this connection it should be said that all clays becoming dense at temperatures below 1400°C should possess a decided range of practically constant porosity. This is especially necessary where the drop in porosity or its equivalent, the rate of shrinkage, is quite rapid. Clays which, upon reaching the state of maximum density, immediately overfire should be ruled out at once, excepting those cases where the overfiring begins at 1425°C or higher. Since these temperatures are already quite high, any overburning at this point is not of serious significance. This is especially true owing to the fact that in all these bodies a certain degree of solution of the refractory grog occurs which will raise the overfiring limit. At the same time the grog content in itself operates against the formation of a vesicular structure. However, we are here concerned with a comparison of the clays. A material overfiring at a high temperature is certainly to be preferred to one reaching this stage at a lower temperature.

Thus, three classes of useful clays are to be distinguished: First, clays burning dense at about 1150°C and showing no evidence of overfiring at 1400°C . This class, provided it possesses the other requisite physical properties, is particularly suited for the manufacture of graphite crucibles used in brass melting. Second, clays burning dense around 1275°C and not overfiring at 1400°C or higher. These clays are adapted for crucibles used in steel melting. When these clays do not overfire before 1425°C , they also become valuable for glass refractories. Third, clays which possess good strength, but do not vitrify at the low temperatures, becoming dense only at 1425°C or higher. These clays, overfiring at about 1450°C or higher, are particularly useful for the purposes of the glass industries. The unsuitable clays are those which become dense anywhere between 1150°C and 1300°C , but possess either no well-defined range between this temperature and that of overfiring or only a short one.

TABLE 1

Lab- ora- tory No.	Source	Water, in terms of dry weight	Water, in terms of true clay volume	Shrink- age in terms of true clay volume	Pore water, in terms of true clay volume	Ratio pore water to shrink- age water	Shrink- age in terms of total water	Appar- ent specific gravity of dried clay	Shrink- age by volume, in terms of total volume	Time of slak- ing	Modu- lus of rupture of dried clay	Modu- lus of rupture of mixture of 1 clay: 1 sand	Remarks
		Per cent	Per cent	Per cent	Per cent		Per cent	Per cent		Min- utes	Lbs./in. ²	Lbs./in. ²	
1	English ball clay.....	44.90	116.0	64.6	51.4	0.79	50.6	1.69	43.30	30	376	323	Good plasticity.
2	Klugeberg, marked A. T.....	39.68	104.0	66.4	37.6	.57	63.8	1.79	42.58	78	345	381	Inclined to crack in drying.
3	New Jersey.....	31.23	81.9	48.3	33.6	.69	58.9	1.90	35.01	12	475	255	Warms and cracks in drying.
4	From a St. Louis (Mo.) firm.....	31.14	80.7	51.5	29.2	.57	63.8	1.94	38.42	52	838	399	No cracking or warping.
5	Klugeberg, marked E. T.....	50.66	132.3	84.8	47.5	.56	64.1	1.70	55.05	108	230	363	No difficulty in drying. Sticky and cracks in drying. Specimens checked.
6	From a St. Louis (Mo.) firm.....	43.63	112.0	65.1	46.9	.72	58.1	1.72	43.63	33	328	351	Very fat but dries well.
7	Kentucky ball clay.....	45.28	117.6	57.2	60.4	1.05	49.6	1.55	34.53	9	239	234	Good plasticity; dries well.
8	Southern Ohio.....	22.08	58.2	32.2	26.0	.80	55.3	2.01	24.46	8	479	281	Fair plasticity; dries well.
9	New Jersey plastic clay.....	41.85	108.8	49.4	59.4	1.20	45.4	1.56	29.86	20	248	185	Good plasticity; lacking in bonding power; dries well.
10	English ball clay.....	40.33	106.5	60.8	45.7	.75	57.1	1.71	39.85	41	366	389	Strong, plastic; dries well.
11	Southern Ohio.....	25.30	66.0	35.9	30.1	.83	54.4	1.94	27.92	83	452	309	Good plasticity; dries well.
12	New Jersey plastic clay.....	34.46	89.7	35.2	54.5	1.54	30.2	1.64	22.12	54	173	94	Fair plasticity; weak.
13	Tennessee.....	37.65	98.2	47.8	50.4	1.05	48.6	1.66	31.01	53	187	199	Very good plasticity; dries well.
14	From a St. Louis (Mo.) firm.....	34.66	90.4	58.7	31.7	.54	63.9	1.90	42.63	117	990	554	Excellent plasticity; dries well.
15	Southern Illinois.....	45.16	117.4	71.0	46.4	.65	60.4	1.67	45.95	54	439	341	Somewhat "greasy," good plasticity; dries well.
16	From a St. Louis (Mo.) firm.....	29.54	72.5	37.2	28.6	.72	58.1	1.91	29.21	103	482	321	Very plastic; dries well.
17	Kentucky ball clay.....	50.85	132.5	77.4	55.1	.51	58.4	1.57	46.80	26	575	351	Good plasticity; dries well.
18	Tennessee ball clay.....	46.10	120.0	61.5	57.4	.65	57.2	1.50	37.96	183	359	362	Very plastic; warps; excellent bonding power.
19	Tennessee.....	44.73	116.3	58.5	57.4	.97	50.6	1.56	35.27	27	387	282	Good plasticity; dries well.
20	Southern Ohio.....	26.98	68.3	39.7	28.6	.72	58.1	1.91	29.21	103	482	321	Very plastic; warps somewhat.
21	Southern Ohio, washed.....	26.84	69.5	37.2	32.8	.87	53.5	1.88	26.98	10	328	277	Very plastic; dries well.
22	Maryland.....	38.51	101.9	60.5	40.5	.67	59.0	1.76	40.61	113	328	277	Do.
23	Arkansas.....	23.02	73.3	43.7	31.6	.57	58.0	1.86	32.32	128	817	518	Sticky; cracks in drying.
24	Grossamerode.....	20.64	58.4	26.8	26.6	.60	59.1	1.93	20.37	493	502	466	Very plastic and dries well.
25	Southern Illinois.....	40.98	106.8	60.9	45.9	.75	57.0	1.66	38.81	45	338	262	Do.
26	Northern Illinois.....	19.84	51.6	27.3	24.3	.89	52.8	2.03	21.08	12	442	240	Somewhat "greasy," but dries well.
27	St. Louis district.....	25.52	66.0	37.8	28.2	.74	57.2	1.95	28.52	46	489	263	Fair plasticity; dries well.
28	Mississippi.....	31.39	81.6	45.0	36.6	.81	55.1	1.81	31.36	55	645	326	Good plasticity and dries well. Somewhat sticky and slightly inclined to crack.

TABLE 2

No.	Source	1050° C		1075° C		1100° C		1125° C		1150° C	
		Porosity	Volume shrinkage	Porosity	Volume shrinkage	Porosity	Volume shrinkage	Porosity	Volume shrinkage	Porosity	Volume shrinkage
		Per cent	Per cent	Per cent	Per cent	Per cent	Per cent	Per cent	Per cent	Per cent	Per cent
1	English ball clay.....	16.64	24.80	7.30	35.52	1.99	33.84	1.62	35.30	0.19	36.72
2	Klingenberg, A. T.....	26.15	14.80	18.62	5.86	28.85	1.74	30.32	1.83	31.30
3	New Jersey.....	25.15	11.15	21.85	16.75	16.95	21.00	14.40	22.61	9.84	24.90
4	From a St. Louis firm....	23.15	6.15	21.81	9.17	17.85	11.50	18.45	12.42	15.52	13.18
5	Klingenberg, E. T.....	23.92	23.21	6.23	2.90	2.28	38.71	2.86	39.50
6	From a St. Louis firm....	33.40	14.55	30.80	17.80	22.12	25.52	10.33	32.50	8.78	33.95
7	Kentucky.....	37.09	11.49	33.90	16.83	26.02	26.80	21.25	30.90	17.83	34.21
8	Southern Ohio.....	22.83	7.34	18.91	10.10	15.82	12.85	14.35	14.87	12.95	16.06
9	New Jersey.....	40.80	9.92	39.50	12.24	35.20	17.15	27.75	25.32	21.28	30.12
10	English ball clay.....	20.70	20.62	11.89	26.28	3.45	30.00	1.49	31.45	1.28	32.51
11	Southern Ohio.....	23.55	6.66	21.72	9.97	17.61	11.95	15.01	15.61	12.05	17.95
12	New Jersey.....	40.40	6.13	39.20	6.76	37.90	8.68	33.90	12.86	28.38	19.30
13	Tennessee ball clay.....	33.60	7.50	30.80	10.26	27.50	15.71	22.55	21.85	19.10	25.35
14	From a St. Louis firm....	24.75	7.92	21.95	9.90	18.85	13.05	16.48	15.09	11.52	17.25
15	Southern Illinois.....	34.61	12.30	33.20	14.42	30.70	17.70	21.85	27.02	10.85	35.15
16	From a St. Louis firm....	24.28	15.88	10.57	7.23	4.89
17	Kentucky ball clay.....	37.80	13.05	30.90	22.70	22.28	30.23	18.25	33.30	16.48	33.25
18	Tennessee ball clay.....	37.50	12.84	28.70	23.45	20.75	31.14	16.95	34.72	13.90	37.10
19	Tennessee.....	35.48	17.90	26.55	25.60	19.03	32.20	16.50	34.82	12.71	36.55
20	Southern Ohio.....	22.30	8.27	18.20	13.62	15.12	16.95	14.08	18.40	11.82	20.30
21	Southern Ohio, washed..	25.48	7.08	22.43	11.02	19.15	14.50	16.76	16.30	16.38	17.12
				1090° C				1120° C			
22	Maryland.....	21.80	18.22	17.13	23.55	10.90	27.52
23	Arkansas.....	28.95	28.50	28.00	.72	26.92	.92	26.82	2.13
				1090° C							
24	Grossalmerode.....	26.06	4.14	24.92	4.97	22.52	7.59
25	Southern Illinois.....	37.30	13.50	33.90	16.12	28.89	21.60
26	Northern Illinois.....	23.12	7.42	22.80	7.78	20.86	10.00	18.95	11.60	16.37	14.11
27	St. Louis district.....	24.90	8.70	23.35	10.34	21.10	13.62	19.75	16.19	17.05	19.30
28	Mississippi.....	30.32	9.75	29.80	9.90	25.30	14.15	20.80	18.62	15.96	22.80

TABLE 2—Continued

No.	Source	1175° C		1200° C		1230° C		1260° C		1290° C	
		Porosity	Volume shrinkage	Porosity	Volume shrinkage	Porosity	Volume shrinkage	Porosity	Volume shrinkage	Porosity	Volume shrinkage
		Per cent	Per cent	Per cent	Per cent	Per cent	Per cent	Per cent	Per cent	Per cent	Per cent
1	English ball clay.....	0.31	36.90	0.68	36.63	0.69	36.52	0.50	36.60	0.77	35.91
2	Klingenberg, A. T.....	2.50	31.71	1.54	32.65	1.3672	33.18	1.04
3	New Jersey.....	5.80	26.95	1.83	27.28	2.83	25.05	5.66	19.95	11.01	16.78
4	From a St. Louis firm....	13.32	13.88	11.95	15.46	9.45	17.82	7.38	19.33	2.66	20.30
5	Klingenberg, E. T.....	2.76	3.35	38.60	3.94	39.70	2.96
6	From a St. Louis firm....	3.95	35.50	1.23	36.45	2.00	37.92	2.44	38.60	1.76	39.30
7	Kentucky.....	17.05	35.40	12.95	37.01	6.13	39.00	.19	41.20	.81	41.75
8	Southern Ohio.....	12.02	17.15	11.56	17.10	8.66	17.38	8.71	17.80	6.82	18.06
9	New Jersey.....	20.35	16.45	33.50	14.09	35.60	11.46	38.08	8.50	38.50
10	English ball clay.....	1.43	33.80	.92	32.80	1.11	33.10	.97	32.05	31.10
11	Southern Ohio.....	10.26	18.21	9.71	19.78	6.90	20.83	3.14	21.69	.49	21.80
12	New Jersey.....	27.69	20.89	27.10	22.08	22.30	25.40	19.95	28.00	16.56	29.55
13	Tennessee ball clay.....	12.65	28.95	8.13	31.42	4.04	32.70	.71	34.41	.34	35.10
14	From a St. Louis firm....	2.12	18.27	1.02	18.96	1.12	19.56	2.75	18.87	2.82	12.15
15	Southern Illinois.....	6.71	34.80	3.85	35.50	2.11	35.85	2.34	38.90	2.02	38.85
16	From a St. Louis firm....	1.91	1.39	1.37	2.29	2.61
17	Kentucky ball clay.....	13.90	34.70	8.43	37.50	3.46	39.02	2.45	40.55	.98	41.25
18	Tennessee ball clay.....	9.00	36.90	3.77	39.12	40.50	2.29	41.80	1.71	42.75
19	Tennessee.....	4.05	39.01	1.38	1.07	40.80	1.32	39.50	.72	40.20
20	Southern Ohio.....	9.75	20.95	7.39	22.32	3.58	23.75	1.19	24.20	5.66	20.90
21	Southern Ohio, washed..	16.20	18.25	14.50	20.20	12.22	22.08	7.25	25.12	.19	26.02
						1225° C		1250° C		1285° C	
22	Maryland.....	4.93	29.01	2.14	30.32	1.27	30.55	.60	31.40	1.17	32.30
23	Arkansas.....	26.40	1.73	25.45	2.18	25.40	1.92	25.40	1.93	25.60	1.60
24	Grossalmerode.....	21.70	7.59	20.50	7.84	19.45	7.43	18.69	8.12	16.90	8.55
25	Southern Illinois.....	24.48	26.40	15.00	32.30	13.27	32.80	9.45	34.05	5.83	35.40
26	Northern Illinois.....	16.37	14.16	15.13	14.75	14.05	14.65	13.13	15.35	11.10	16.40
27	St. Louis district.....	16.35	18.76	15.45	19.60	13.72	21.10	11.61	22.30	8.96	23.25
28	Mississippi.....	15.76	23.30	14.10	23.10	12.92	23.30	9.87	24.20	5.95	25.65

TABLE 2—Continued

No.	Source	1320° C		1350° C		1400° C		1425° C		1450° C	
		Porosity	Volume shrinkage	Porosity	Volume shrinkage	Porosity	Volume shrinkage	Porosity	Volume shrinkage	Porosity	Volume shrinkage
		Per cent	Per cent	Per cent	Per cent	Per cent	Per cent	Per cent	Per cent	Per cent	Per cent
1	English ball clay.....	2.20	34.35	2.31	31.32						
2	Klingenberg, A. T.....	1.49	32.32	1.56	29.75	1.59	30.70	1.48	26.64	3.93	16.35
3	New Jersey.....		10.83		7.78						
4	From a St. Louis firm.....	2.09	19.34	13.75	12.78						
5	Klingenberg, E. T.....	2.19	38.00	2.47		2.42	36.40	3.23		3.53	26.85
6	From a St. Louis firm.....	1.85	38.65	2.08	38.30	2.09	39.55	1.85	38.22	4.61	34.05
7	Kentucky.....	.97	42.75	.81	42.60	.95	42.80	.33	42.10	3.30	37.62
8	Southern Ohio.....	2.50	18.18	.52	13.78	4.56	14.21	6.01	9.08	5.60	
9	New Jersey.....	2.97	40.10	1.16	40.35	.71	40.25	1.33	37.90	5.45	31.25
10	English ball clay.....	1.38	27.87	1.59	28.65	.82	28.50	2.34	24.90	3.03	19.95
11	Southern Ohio.....	.09	20.65	2.83	16.20						
12	New Jersey.....	11.88	32.15	8.60			33.45	6.68	35.00	.84	36.35
13	Tennessee ball clay.....	.17	35.10	.38	34.10	1.28	33.10	.48	28.50	4.89	20.20
14	From a St. Louis firm.....	10.82	8.14	16.90	.75						
15	Southern Illinois.....	2.07	39.40	2.27	39.10	2.53	40.00	2.15	38.90	2.72	35.15
16	From a St. Louis firm.....	5.62		6.01							
17	Kentucky ball clay.....	1.18	41.25	1.48	42.02	.84	40.80	2.76	39.75	6.00	37.90
18	Tennessee ball clay.....	2.34	42.90	1.99	40.95	3.02	39.10	3.22	35.70	4.45	34.50
19	Tennessee.....	2.15	39.30	1.14	39.15	.82	38.45	1.39	36.10	2.85	35.35
20	Southern Ohio.....	7.64	18.23	12.95	13.62						
21	Southern Ohio, washed..	.71	27.60	1.46	26.32	3.56	25.41	7.02	17.95		12.92
		1315° C				1390° C		1420° C			
22	Maryland.....	1.47	32.35	1.53	30.70	2.44	28.85	5.92	22.25	7.95	18.60
23	Arkansas.....	24.95	1.82	25.05	1.81	25.02	1.94	24.40	2.12	23.90	2.24
24	Grossalmerode.....	15.53	9.67	14.10	9.68	12.25	10.70	11.85	10.60	6.95	8.64
25	Southern Illinois.....	5.09	38.12	3.30	38.40	2.86	38.60	3.13	38.40	3.92	37.38
26	Northern Illinois.....	9.44	17.25	7.98	17.38	5.75	19.23	4.32	19.65	3.08	18.85
27	St. Louis district.....	6.93	24.95	3.67	25.20	2.47	24.35	3.48	23.30	7.26	19.35
28	Mississippi.....	1.93	27.55	1.55	27.95	1.81	28.40	1.77	27.65	2.92	24.65

TABLE 2—Continued

No.	Source	1475° C		1500° C		Softening temperature in cones	Remarks
		Porosity	Volume shrinkage	Porosity	Volume shrinkage		
		Per cent	Per cent	Per cent	Per cent		
1	English ball clay.....					31½	Overfired at 1320°.
2	Klingenberg, A. T.....	6.02		3.79		32	Overfired at 1450°. Sensitive to sudden cooling.
3	New Jersey.....					27½	Begins to overfire at 1230°.
4	From a St. Louis firm.....					27	Overfired decidedly at 1350°.
5	Klingenberg, E. T.....			3.79		32	Cracked in drying and burning. Overfired at 1450°.
6	From a St. Louis firm.....	6.54	25.32	7.01		32	Overfired at 1450°.
7	Kentucky.....	4.88	32.90	7.13		32½	Do.
8	Southern Ohio.....					31	Begins to overfire at 1400°.
9	New Jersey.....	3.85	25.30	5.30	23.80	32	Overfired at 1450°.
10	English ball clay.....	3.05		6.95		32	Overfired at 1425°.
11	Southern Ohio.....					30½	Overfired at 1350°.
12	New Jersey.....	.15	34.00	1.77	29.78	32	Overfired at 1500°.
13	Tennessee ball clay.....	2.90	16.28	6.03		32	Overfired at 1425°.
14	From a St. Louis firm.....					27	Overfired at 1320°.
15	Southern Illinois.....	4.38	28.35	5.82	26.85	32	Overfired at 1450°.
16	From a St. Louis firm.....						Overfired at 1320°.
17	Kentucky ball clay.....			4.85	35.60	32	Overfired at 1450°.
18	Tennessee ball clay.....			5.80	33.40	+32	Overfired at 1425°.
19	Tennessee.....			5.18		+32	Overfired at 1450°.
20	Southern Ohio.....					30½	Overfired at 1290°.
21	Southern Ohio, washed.....					21½	Overfired at 1400°.
1480° C							
22	Maryland.....	6.95	19.00	4.90	18.65	31	Begins to overfire at 1390°.
23	Arkansas.....	22.55	2.69			29	Does not overfire at 1475°+.
1505° C							
24	Grossalmerode.....	11.90	4.73	26.20	11.1	29	Overfired at 1480°.
25	Southern Illinois.....	4.54	34.50	10.25	30.80	+32	Overfired at 1475°.
1470° C							
26	Northern Illinois.....	1.92	18.90			29	Not yet overfired at 1475°.
27	St. Louis district.....	10.50	18.10			31	Overfired at 1450°.
28	Mississippi.....	8.63	19.95			30	Begins to overfire at 1450°.

IV. DISCUSSION OF THE INDIVIDUAL CLAYS

No. 1, English Ball Clay.—This clay possesses sufficient strength to be classed as a bond clay, its modulus being 376 pounds per square inch. It vitrifies at 1150°C and overfires distinctly at

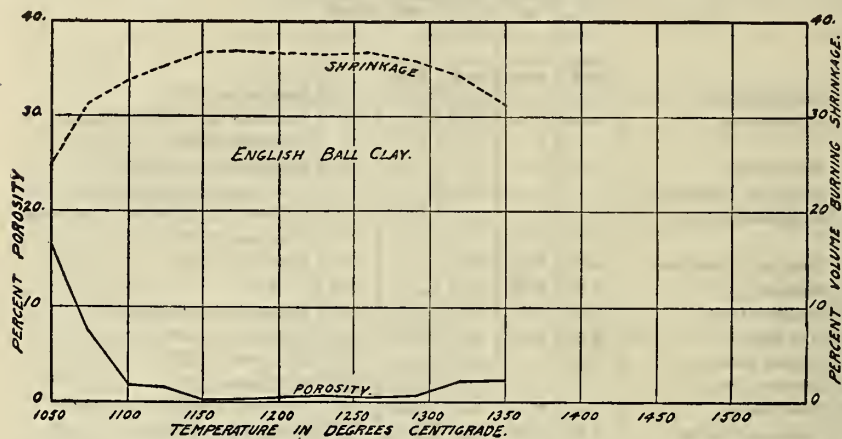


FIG. 1.—Diagram showing contraction with temperature of English ball clay (No. 1)

1320°C , but not seriously. Its porosity and volume changes with temperature are shown in Fig. 1. From the contraction curve it appears, as shown by the downward trend of the curve, that swelling begins at about 1300°C . The material, therefore, is not prom-

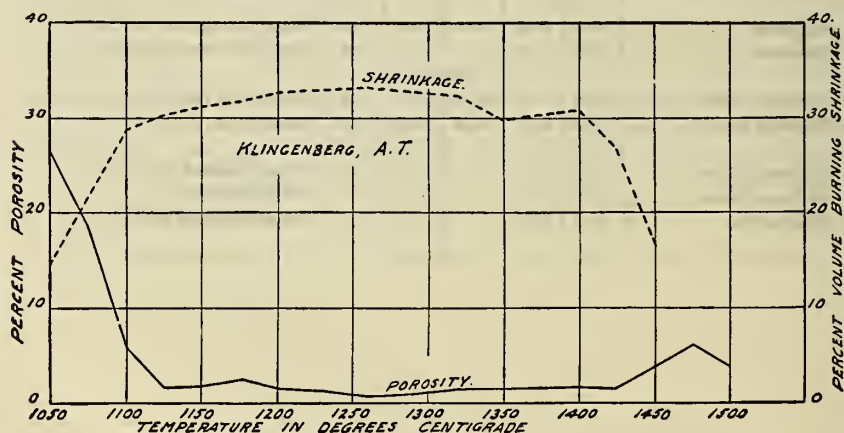


FIG. 2.—Diagram showing contraction with temperature of Klingenberg clay, A. T. brand

ising for steel-melting crucibles and for glass refractories, though it might be satisfactory for brass-melting crucibles.

No. 2, Klingenberg, A. T.—The bonding power of this clay is not of an extraordinary quality and, in fact, is inferior to that of

some American clays. In addition, its tendency to crack badly in drying is an undesirable feature. It has, of course, ample mechanical strength for the purpose for which it is used, the making of graphite crucibles. From Fig. 2 it will be seen that it vitrifies at 1125°C and remains remarkably constant in structure up to 1425°C . At this point overfiring begins, as is shown particularly by the volume curve, which indicates decided bloating, so that at 1450°C the clay has about the same volume it had at 1050°C before vitrification took place. At 1450°C it is, therefore, decidedly overfired. However, its excellent burning behavior is apparent from the long temperature range. It would not be a satisfactory glass refractory. One disadvantage of this material is its extreme sensitiveness to sudden heating and cooling as it shatters very readily under such conditions. Its softening temperature is satisfactory.

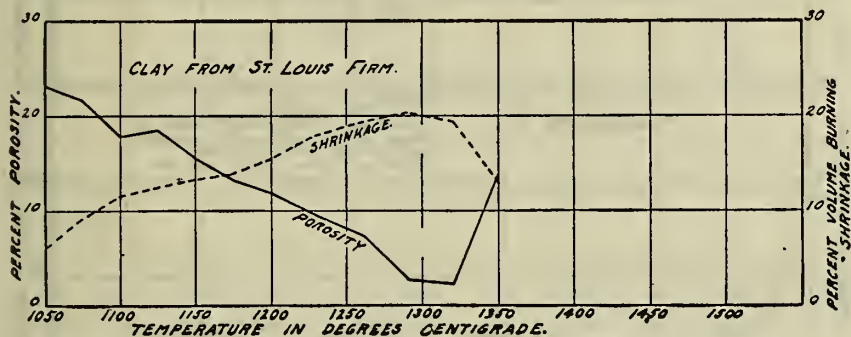


FIG. 3.—Diagram showing contraction with temperature of clay from St. Louis firm (No. 4)

No. 3, New Jersey Clay.—This clay is of a siliceous nature, and, while it possesses excellent strength in the unmixed state, it is somewhat deficient in bonding power, as indicated by its low modulus when admixed with sand, 255 pounds per square inch. In burning it reaches the vitrified state at 1200°C . and shows evidence of overfiring by decided swelling at 1230°C . These results, together with its low softening point, should exclude it from use as a high-grade bond clay.

No. 4, Clay from a St. Louis Firm.—This material is an excellent one from the standpoint of plasticity, bonding power, and strength. It shows a modulus of 399 pounds per square inch. It becomes dense at 1290°C , but overfires at 1320°C , and at 1350°C it has developed a decided vesicular structure, indicated both by the volume and porosity changes, as shown in Fig. 3. Its softening point is that of cone 27. The material must, therefore, be rejected as a high-grade bond clay.

No. 5, *Klingenberg, E. T.*—This clay is of a sticky nature and possesses good plasticity and bonding power, its modulus being 363 pounds per square inch. It has a strong tendency to check and crack in drying. In burning it becomes dense at 1100°C , and it shows an extraordinary temperature range up to 1400°C . It begins to bloat at this temperature although its porosity is not decidedly increased, even at 1450°C . As is seen in Fig. 4, the volume change is especially useful in indicating the structural changes taking place. It is interesting also to observe the high resistance of the dried clay to the disintegrating action of water.

No. 6, *Clay from a St. Louis Firm.*—The clay is a satisfactory one from the standpoint of its physical properties in the raw state. It shows a modulus of rupture of 351 pounds per square inch. It becomes quite dense at 1200°C and starts to overfire at about

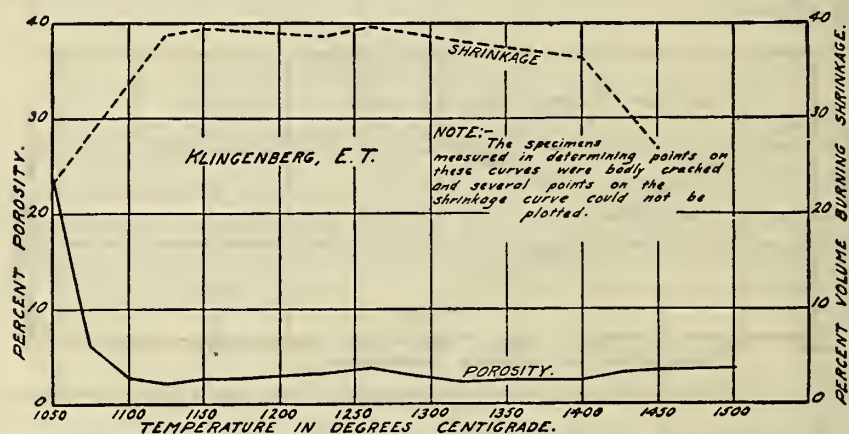


FIG. 4.—Diagram showing contraction with temperature of Klingenberg clay, E. T. brand

1430°C , this condition being distinctly shown at 1450°C . It shows, thus, an excellent temperature range. Its propensity to bloat at this temperature is quite evident. Its refractoriness is satisfactory, the softening point being equivalent to that of cone 32. The clay seems very promising as a crucible material.

No. 7, *Kentucky.*—This material is very plastic, but is lacking in bonding power, as indicated by the low modulus, 234 pounds per square inch. This might be inferred also from the high ratio of pore to shrinkage water, which is 1.05. The specific gravity, 1.55, is below the average of such clays. The clay vitrifies to a dense structure at about 1260°C and remains quite constant up to 1425°C , where it begins to overfire. At 1450°C it shows distinct evidence of this change. (See Fig. 5.) Its refractoriness, corresponding to that of cone 32, is satisfactory. This clay could be

used in conjunction with a stronger clay as a bonding material for crucibles, but would hardly be suitable for this purpose if used alone. It might be used also for glass refractories with other clays of somewhat different properties. The high porosity of the clay at 1050°C , 37 per cent, is indicative of its open structure in the

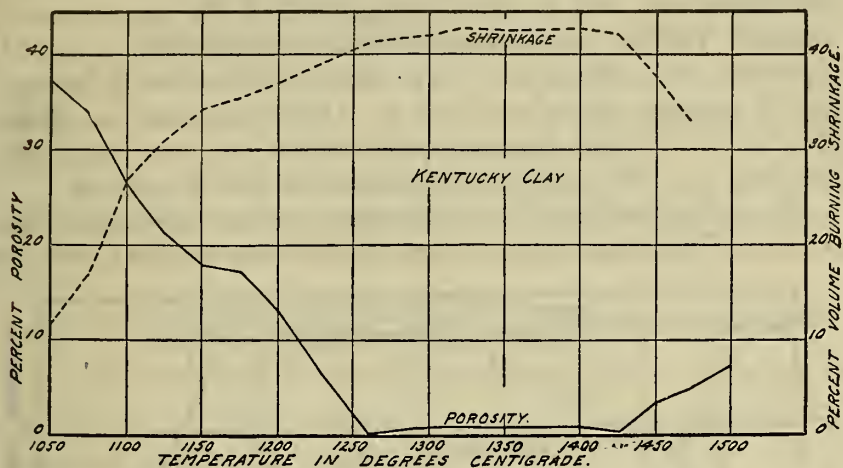


FIG. 5.—Diagram showing contraction with temperature of Kentucky ball clay (No. 7)

dried state and explains the ready disintegration of the raw clay in water.

No. 8, *Southern Ohio*.—This clay, though quite plastic, is somewhat deficient in bonding power. Its modulus with sand is 281 pounds, but its strength without admixture is considerable, 479

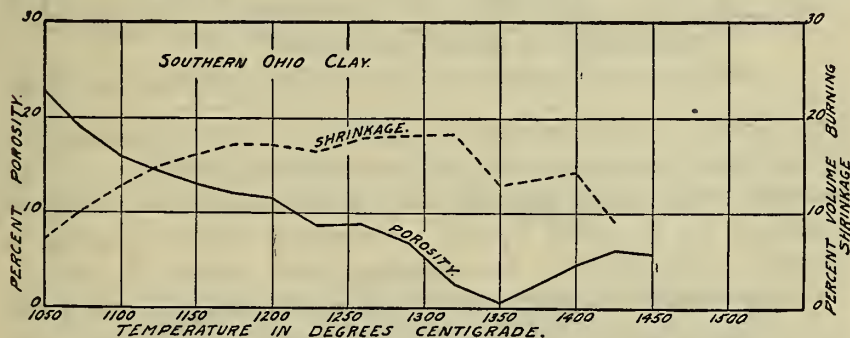


FIG. 6.—Diagram showing contraction with temperature of bond clay from southern Ohio (No. 8)

pounds. Its specific gravity in the dried state is above the average and indicates a dense structure, which is verified by its low porosity, 22.83 per cent at 1050°C . The clay burns to dense vitrification at 1350°C and begins to overfire soon after this temperature has been reached. At 1400°C it is distinctly vesicular. (See Fig. 6.)

It softens at cone 31. The material is not of the highest type, though it could be used in a mixture with other clays.

No. 9, New Jersey.—The low strength of this clay in the dry state would prohibit its use as a bond clay by itself. It has, however, good burning qualities, which would render it suitable for admixture with one or more strong clays of the dense-burning variety. The clay is of a siliceous nature and possesses at 1050°C a porosity of 40.80 per cent. Its rate of vitrification is gradual, and it becomes dense at 1350°C . Overfiring starts at about 1425°C . Expansion becomes quite evident at this temperature. (See Fig. 7.) The softening temperature is that of cone 32.

No. 10, English Ball Clay.—This clay, with its satisfactory proportion of shrinkage water to true clay volume 60.8 per cent, its

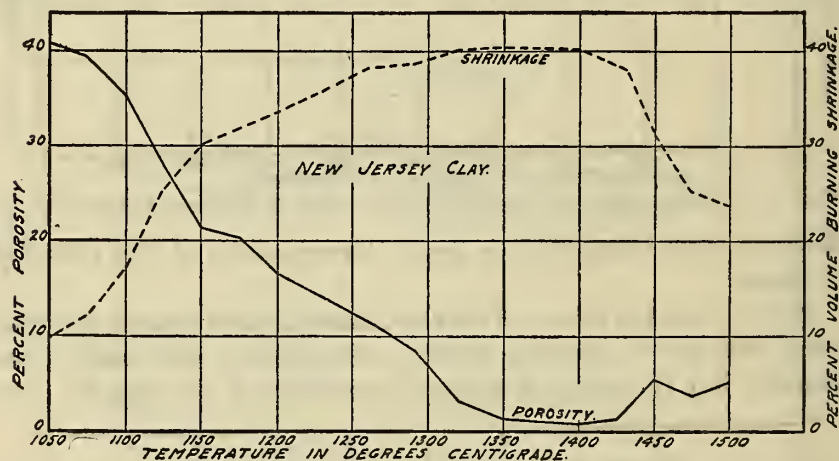


FIG. 7.—Diagram showing contraction with temperature of a New Jersey clay (No. 9)

pore-shrinkage water ratio of 0.75 and modulus of 389 pounds per square inch, possesses all the good qualities of a bond clay. This material burns quite dense at 1125°C and shows no evidence of overfiring up to about 1415°C . Overfiring is not serious up to 1450°C . (See Fig. 8.) Its softening point is that of cone 32. This clay should be a useful one for the crucible industry and would be a desirable constituent of a glass-pot batch, especially for melting corrosive glasses where a dense pot structure is required.

No. 11, Southern Ohio.—This clay is somewhat similar to sample No. 8.

No. 12, New Jersey.—This clay is of a siliceous character and is lacking in bonding power to such an extent that it would be

ruled out from the bond-clay class. Its firing behavior is that of a siliceous clay, low in fluxes. It becomes very dense at 1475°C

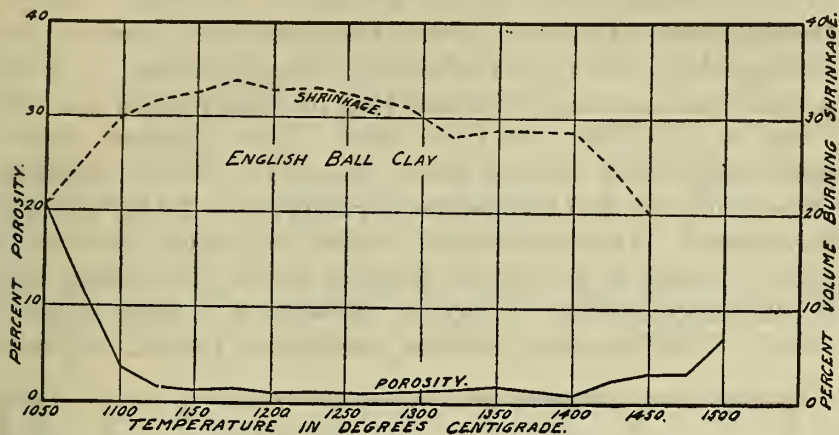


FIG. 8.—Diagram showing contraction with temperature of an English ball clay (No. 10)

and begins to overfire beyond this point. (See Fig. 9.) Its softening point is that of cone 32.

No. 13, *Tennessee*.—This clay, although of excellent plasticity, is lacking in bonding power, as indicated by its modulus of 200

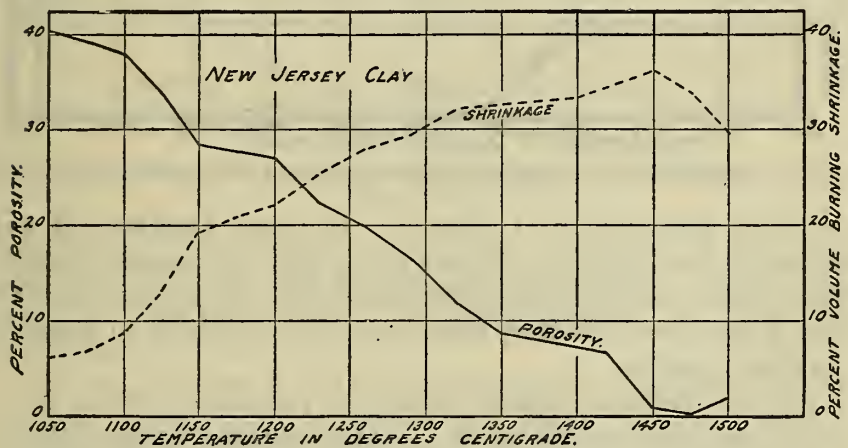


FIG. 9.—Diagram showing contraction with temperature of a New Jersey plastic clay (No. 12)

pounds. At 1050°C it has a porosity of 33.5 per cent and vitrifies gradually, reaching maximum density of structure at about 1260°C . Practically constant porosity is maintained up to about 1425°C

when overfiring begins. (See Fig. 10.) At this point expansion of the clay volume is quite evident. The softening temperature of the material is that of cone 32. In spite of the low bonding power of the clay, it would be useful when admixed with stronger clays, owing to its satisfactory firing behavior. It would probably be better suited for steel than for brass melting crucibles.

No. 14, Clay from a St. Louis Firm.—This clay shows remarkable strength and bonding power, its ratio of pore to shrinkage water being 0.54 and its modulus of rupture 554, the highest of all clays tested. At the same time, it offers no difficulty in drying, a point in which it is decidedly superior to the Klingenberg clay. It vitrifies completely at 1200°C , although it is quite dense at 1175°C . The material, however, overfires at 1320°C and has a

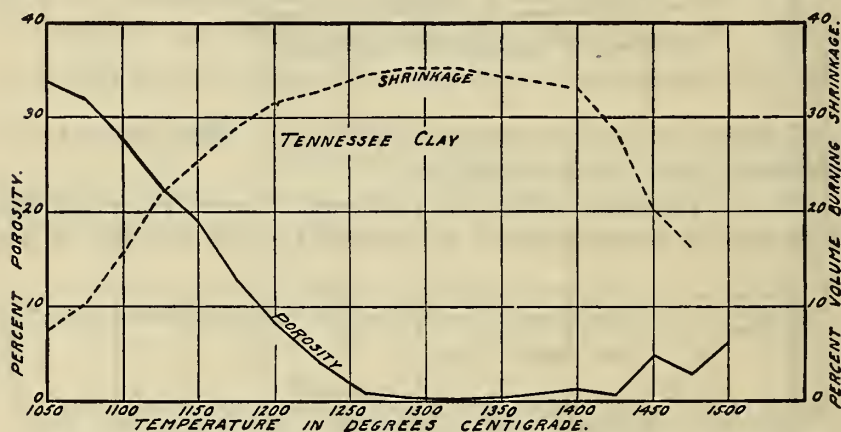


FIG. 10.—Diagram showing contraction with temperature of a Tennessee ball clay (No. 13)

softening temperature of cone 27. The clay, therefore, is not suited for steel-melting crucibles or for glass refractories, though it should be useful for brass-melting work. By admixture with one or two more refractory clays it should be possible to improve its firing qualities.

No. 15, Southern Illinois.—This clay possesses excellent plasticity and good bonding power. Its pore-shrinkage water ratio is 0.65 and its modulus 341 pounds. The porosity at 1050°C is 34.5 per cent, and the clay becomes dense, though not completely vitrified, at about 1230°C . Overfiring does not begin until a temperature of 1450°C has been reached. The temperature range of this clay is, therefore, a very long one. Overfiring does not take place quickly, but evidently is a gradual process. (See Fig. 11.) The softening point is that of cone 32. The clay is un-

questionably one of the best bond clays examined, especially for glass refractories.

No. 16, Clay from a St. Louis Firm.—This clay possesses good plasticity and bonding power, since its modulus is 351 pounds. In burning, however, it overfires at 1320°C and for this reason can not be considered of particular promise.

No. 17, Kentucky Ball Clay.—This clay possesses excellent working qualities and good strength. Its shrinkage water content is very high, being 77.4 per cent, in terms of the true-clay volume; its porosity-shrinkage water ratio is 0.71 and its modulus 362. Its porosity at 1050°C is 37.8 per cent, and it burns to complete vitrification at about 1290°C . It begins to overfire at 1400°C , but this change is a gradual one. Its softening tem-

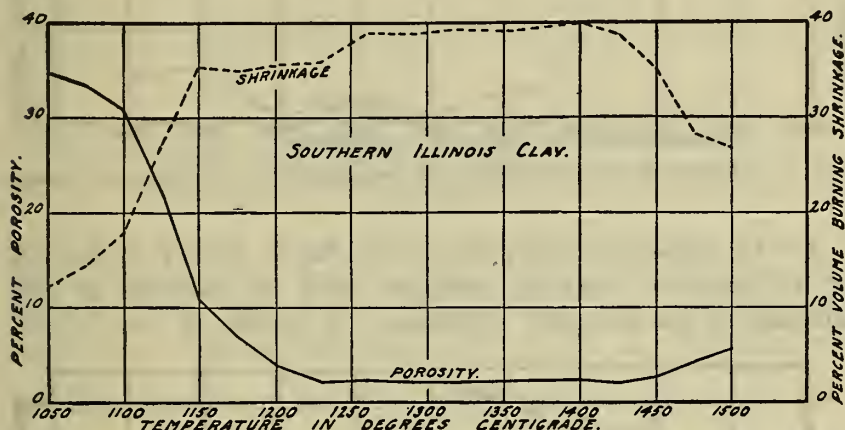


FIG. 11.—Diagram showing contraction with temperature of a bond clay from southern Illinois (No. 15)

perature is that of cone 32. The clay, therefore, is an excellent bond clay, especially suitable for steel-melting crucibles and also for glass refractories. Its firing behavior is illustrated graphically in Fig. 12.

No. 18, Tennessee Ball Clay.—Although this material possesses excellent plasticity, it is somewhat deficient in bonding power, as indicated by its high pore-shrinkage water ratio, 0.95, and its low modulus, 228 pounds. On the other hand, its firing behavior is excellent. It vitrifies at about 1230°C from a porosity of 37.50 per cent at 1050°C . It remains very constant in structure till 1400°C is reached, when it begins to overfire very gradually. It still possesses a good structure at 1450°C . The softening point corresponds to that of cone 32+. It is undoubtedly a valuable

clay, chiefly on account of its good firing qualities. It is especially suitable for glass refractories, but for crucible work it requires admixture with a somewhat stronger clay. The firing qualities of this material are illustrated in Fig. 13.

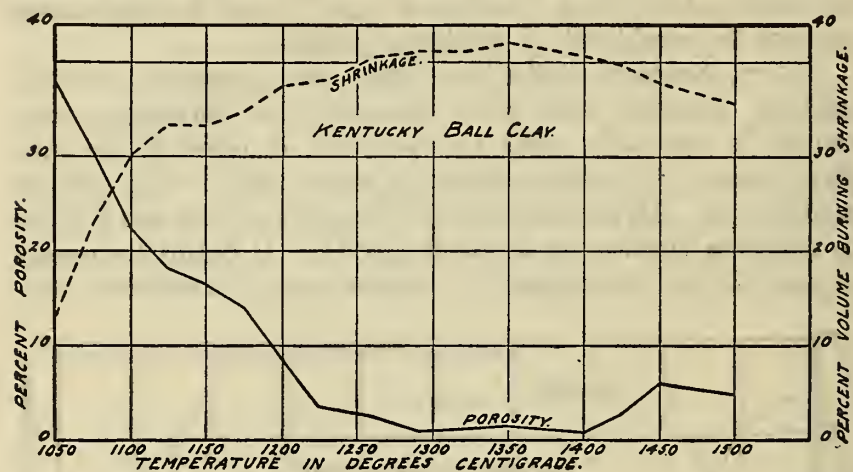


FIG. 12.—Diagram showing contraction with temperature of a ball clay from Kentucky (No. 17)

No. 19, *Tennessee Ball Clay*.—This clay is similar to No. 18, It is, however, decidedly stronger, since its modulus is 282, although it has a smaller shrinkage. It vitrifies at 1200°C and

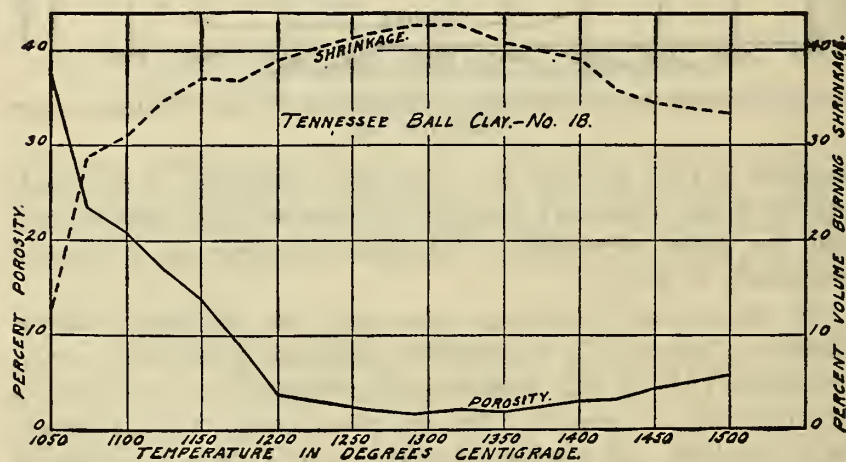


FIG. 13.—Diagram showing contraction with temperature of a Tennessee ball clay (No. 18)

does not begin to overfire before 1425°C. At 1450°C it still shows a good structure. The overfiring takes place gradually, as is seen from Fig. 14. Its softening temperature is about cone 32.

What has been said of the previous clay applies also to this material, though it might be said to be superior to No. 18.

No. 20, Southern Ohio.—This clay is very plastic and possesses satisfactory bonding power. Its pore-shrinkage water ratio is 0.72 and its modulus 321. Its water content is considerably

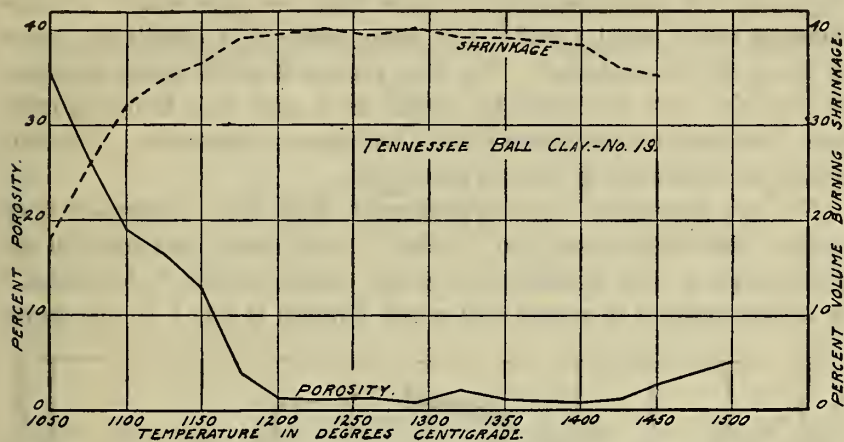


FIG. 14.—Diagram showing contraction with temperature of a Tennessee ball clay (No. 19)

below the average values holding for the other clays, since it is only 39.7 per cent of the true-clay volume. For this reason the density of the molded clay is quite high, the specific gravity being 1.91. The porosity at 1050° C is only 22.30 per cent, and

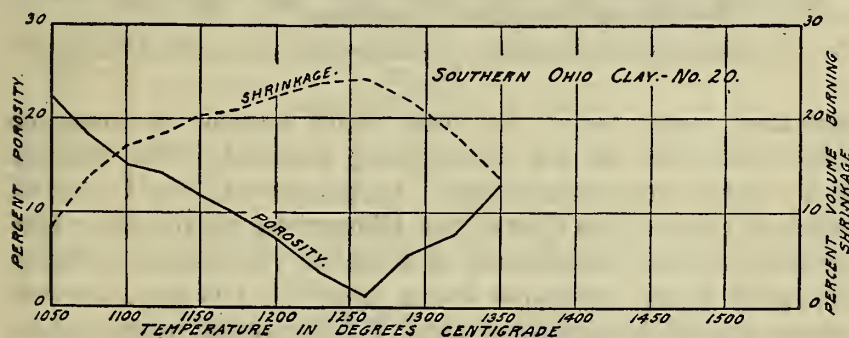


FIG. 15.—Diagram showing contraction with temperature of a southern Ohio bond clay (No. 20)

it vitrifies completely at 1260° C, beginning to overfire immediately. (See Fig. 15.) The softening point is that of cone 30½. It cannot be considered a bond clay of the highest type in view of these results, and, in any event, it should not be used alone, but invariably in conjunction with other clays.

No. 21, Southern Ohio.—This clay is similar to No. 20. It is not quite so strong as the former, indicated both by the higher pore-shrinkage water ratio, 0.87, and by the lower modulus, 277. It vitrifies more gradually, becoming completely dense at 1290°C and overfiring slowly beyond this temperature. (See Fig. 16.) It is interesting to note that no appreciable volume changes occur until 1400°C has been reached, a condition much in favor of the material. For this reason it is distinctly superior to clay No. 20. It should be useful as a part of a bonding mixture for steel-melting crucibles and glass refractories. Its softening temperature is that of cone $31\frac{1}{2}$.

No. 22, Maryland.—In appearances this clay resembles very closely the Klingenberg, A. T. clay. It is black and high in organic matter and exhibits the same characteristic "stickiness." It resists slaking in water still more, though it has a higher pore-

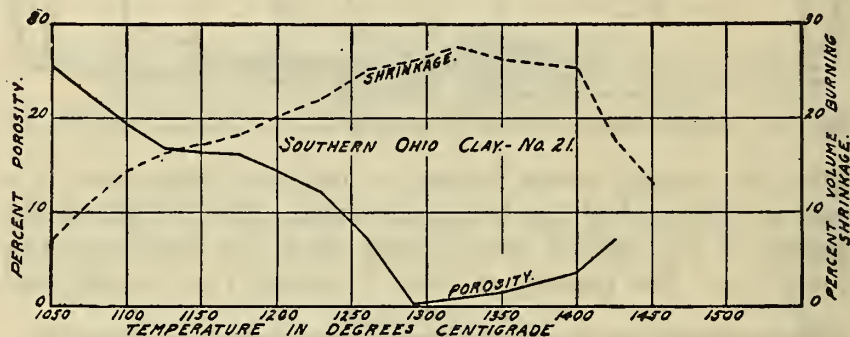


FIG. 16.—Diagram showing contraction with temperature of a southern Ohio bond clay (No. 21)

shrinkage water ratio. Its total water content is somewhat lower than that of the Klingenberg material. The modulus is 518, which is exceedingly high. Its porosity at 1090°C is 21.80, which is greater than that of the Klingenberg at the same temperature, and its temperature of complete vitrification is higher, this point being reached at about 1250°C . The clay, however, reaches a good dense state at 1200°C . Expansion begins to take place somewhat below 1350°C , and this change becomes accelerated markedly at 1400°C , followed by a stage of quiescence. This material evidently becomes quite viscous at temperatures above 1450°C . (See Fig. 17.) The softening point is that of cone 31. It would seem that this clay should be valuable for the crucible industry, though less suitable for glass refractories.

No. 23, Arkansas.—This clay is of the type of the Grossalmerode clay. It is siliceous in character and evidently very

low in fluxing materials. It possesses excellent plasticity and bonding power, being superior in this respect to the German clay. Its required water content is higher than that of the imported material, amounting to 75.3 per cent, in terms of the true-clay volume. Its pore-shrinkage water ratio also more

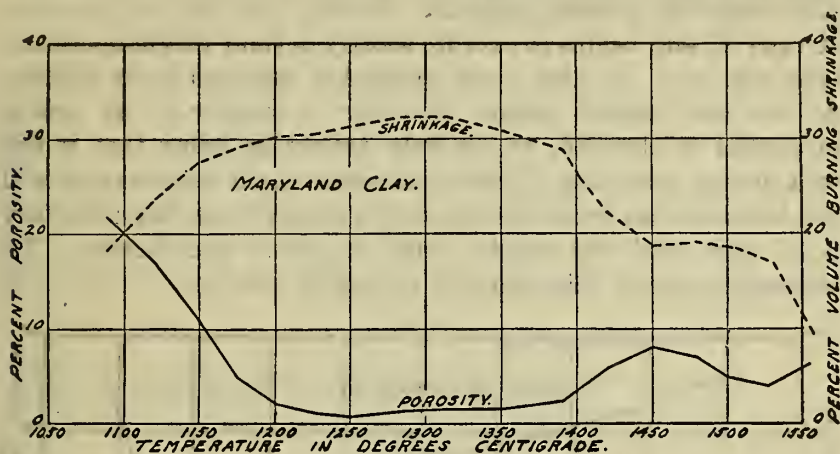


FIG. 17.—Diagram showing contraction with temperature of a Maryland bond clay (No. 22)

favorable, being 0.72. The modulus is 466 pounds. The burning behavior, likewise, is superior to that of the German clay, as may be seen from Fig. 18. It does not vitrify at all within the temperature range employed, its porosity at 1450° C being

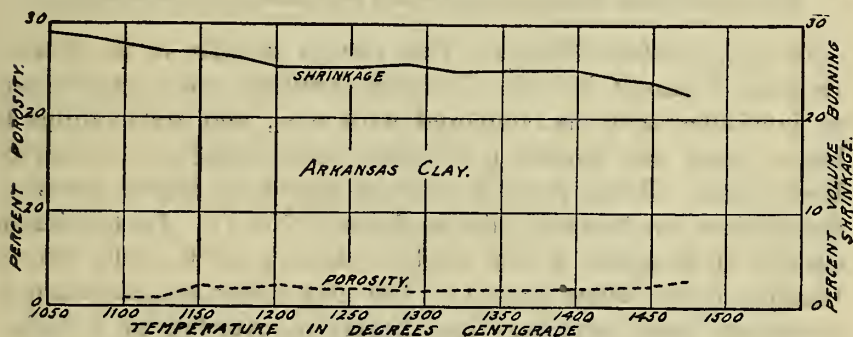


FIG. 18.—Diagram showing contraction with temperature of an Arkansas bond clay (No. 23)

still 23.90 per cent. The volume remains remarkably constant. The softening point is that of cone 29. It is evident that this clay is an excellent glass-pot material, though not adapted to crucible work, except in connection with another stronger but more dense burning refractory material.

No. 24, *Grossalmerode*.—This well-known clay is very plastic, though its pore-shrinkage water ratio is high, 0.99, characteristic of siliceous clays. Its specific gravity in the dried state is high, it being 1.99. Its bonding power is indicated by the modulus, 364 pounds per square inch. It burns to a strong, but still somewhat porous, structure, showing 6.95 per cent porosity, at 1450° C, and begins to overfire shortly beyond this temperature. (See Fig. 19.) At this point expansion becomes quite evident. As has been stated before, this clay is inferior in its general properties to clay No. 23, its only advantage being that it fires to a denser structure. The same result could be obtained with the Arkansas clay by admixture with a denser firing, but refractory, bond clay, and the result would be more satisfactory. The softening point of this material is that of cone 29.

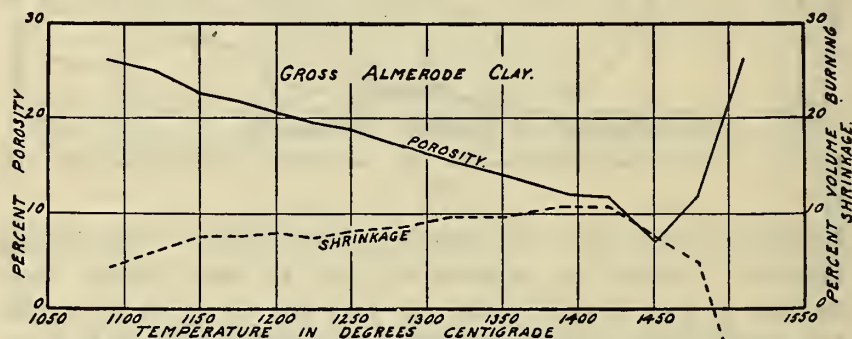


FIG. 19.—Diagram showing contraction with temperature of Grossalmerode clay.

No. 25, *Southern Illinois*.—This clay is similar in its characteristics to sample No. 15. Its pore-shrinkage water ratio is not so favorable, 0.75, as compared with 0.65, and its modulus is lower, being 262 pounds per square inch, though its plasticity is excellent. When fired, it shows a somewhat higher porosity, and it does not become quite as dense as No. 15. Its maximum density of structure is not reached before 1350° C, while No. 15 becomes dense below 1250° C. The clay under consideration is somewhat more refractory and begins to over-fire at a higher temperature. (See Fig. 20.) Its softening point is that of cone 32+. In spite of its lower bonding power, this clay should be very useful as a general refractory bond clay, especially for steel-melting crucibles and glass pots. It should be used in connection with somewhat stronger bond clays.

No. 26, *Northern Illinois*.—This No. 2 fire clay shows the lowest water content of any of these clays. The per cent of shrinkage

water in terms of the true-clay volume is only 27.3 and the pore-shrinkage water ratio is 0.89. The material shows fair plasticity and its modulus is 240. The siliceous character of the clay is indicated by the porosity-temperature diagram (See Fig. 21.)

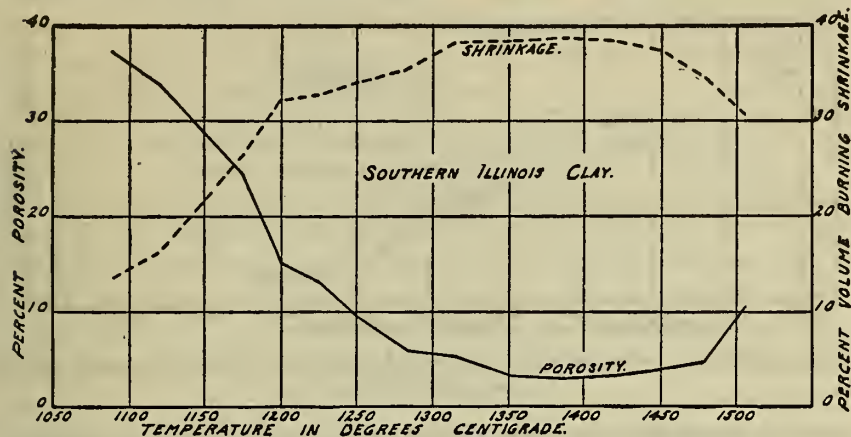


FIG. 20.—Diagram showing contraction with temperature of southern Illinois bond clay (No. 25)

It is of the Grossalmerode type and shows a steady progress of vitrification. Over-firing was not yet observed at 1475° C. From the burning standpoint the material is a very excellent one. The softening point corresponds to that of cone 29. It is evident that this clay is a useful one, especially when blended with such

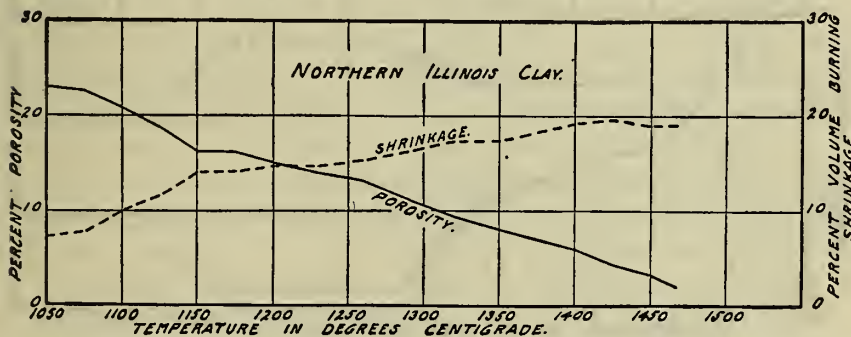


FIG. 21.—Diagram showing contraction with temperature of plastic fire clay from northern Illinois (No. 26)

a material as No. 15. Its primary use would be in connection with glass refractories, although, together with a clay like No. 22, it would produce a good crucible mixture, adjusted to produce the desired density of structure at a lower temperature.

No. 27, St. Louis District.—This is a typical clay from this district, of good plasticity, but somewhat deficient in bonding power. The pore-shrinkage water ratio is 0.74 and the modulus is 263 pounds per square inch. Its porosity at 1050°C is 25 per

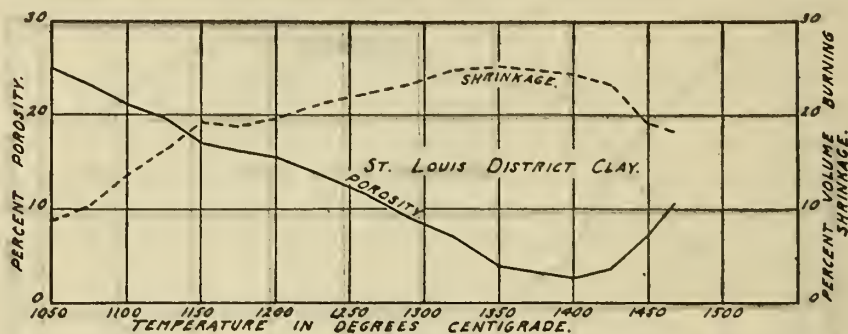


FIG. 22.—Diagram showing contraction with temperature of a band clay from the St. Louis district (No. 27)

cent, and vitrification proceeds uniformly and steadily to a porosity of 2.5 per cent at 1400°C . It does not begin to overfire till 1425°C is reached. (See Fig. 22.) It is, therefore, a very satisfactorily burning material. Here, again, it should be stated that the best results are obtained in admixture of this clay with a clay of

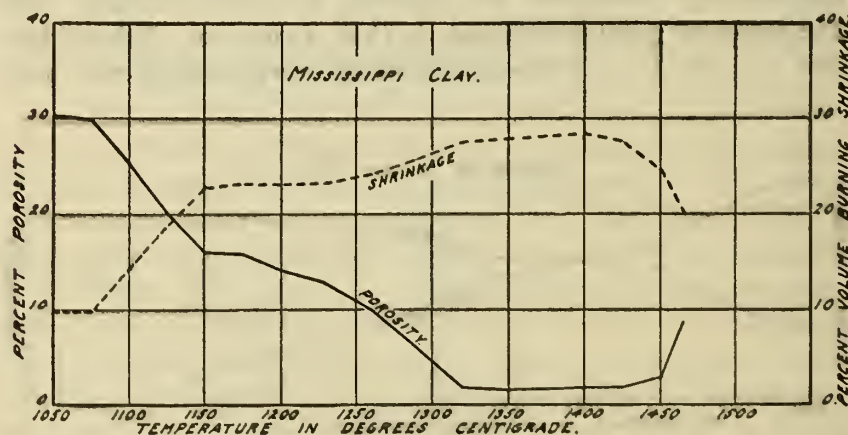


FIG. 23.—Diagram showing contraction with temperature of a bond clay from Mississippi (No. 28)

greater bonding power and supplementing its burning characteristics. The softening point is that of cone 31.

No. 28, Mississippi.—This bond clay is of a slightly "sticky" nature, somewhat inclined to crack in drying. Its pore-shrinkage

water ratio is 0.81, and its bonding power is very acceptable, as indicated by its modulus, which is 326 pounds per square inch. Beginning with a porosity of 30 per cent at 1050° C, it vitrifies quite gradually, becoming dense at 1320° C. This condition is maintained constant up to 1450° C, where overfiring occurs, indicated by expansion on the volume change curve. (See Fig. 23.) The softening point is that of cone 30. The clay should be generally useful as a bonding material.

V. CONCLUSIONS REGARDING AMERICAN BOND CLAYS

The results here given furnish proof for the assertion that we have in the United States clays which make possible the manufacture of the several kinds of refractories without the use of imported materials. The fact should be emphasized that in nearly every case the use of an intimately blended mixture of suitable clays is to be preferred to the use of single clays. In this manner, using such data as have been here presented, it should be possible to produce bodies possessing all the desired properties. Very similar clays should not be worked together. To illustrate this statement, we might say, for instance, that clay No. 23 (Arkansas) should be blended with clay No. 27 (St. Louis district) for glass refractories. In this manner, by the use of clays which show certain contrasts, it would be possible to exercise accurate control over the resulting qualities, and hence to secure the best commercial results. A clay like No. 22 (Maryland) should be supplemented by such clays as Nos. 7 (Kentucky), No. 13 (Tennessee), or Nos. 18 and 19 (Tennessee). Again, No. 14 would be improved by mixture with Nos. 15, 25, or 26 (Illinois). It is evident that in this fashion more or less dense, or, again, open, burning bodies may be produced according to the specific needs of each case. It is very much to be urged that systematic methods of studying these raw materials replace the cut-and-try procedures which are only too common. For glass refractories a siliceous clay should be used as the basis, and this should be reinforced by the addition of suitable dense-burning materials.

It goes without saying that there are many clays of the bond-clay type in the United States. In addition, there are available the plastic kaolins, which, though they would not contribute toward the strength of the body, are very effective in increasing the refractoriness and raising the overfiring temperature. In this laboratory the use of Georgia and Florida kaolins, in percentages up to 20 of the total clay employed, has been found to be very

effective for high-grade bodies. At the prevailing prices of No. 1 bond clays the use of the unwashed Georgia kaolins would not be prohibitive.

Some mistakes have been made in the hurry to develop promising clay properties. These errors consist in including in shipments entirely unsuitable clays adjoining the strata of good clay, poor judgment in differentiating the different clays, the failure to reject obvious impurities, such as pyrites or gypsum, and especially in failing to make a comprehensive and thorough survey of the deposits, both by borings and by the sinking of shafts. As a result, some disappointment has resulted from developments which were very promising in the beginning, but proved unsatisfactory both to the user and the miner. The matter of preliminary clay testing has been practically disregarded entirely, excepting by several well-established firms, and the cost of experimenting in the use of these clays devolved almost entirely upon the user, who in most cases was able to do this only by making up ware, a method of testing which is expensive, to say the least. A few easily made preliminary clay tests would have saved much time, money, and disappointment, inasmuch as they would have eliminated the most undesirable materials.

Part II—THE USE OF BOND CLAYS IN THE MAKING OF GRAPHITE CRUCIBLES AND GLASS REFRACTORIES

I. GRAPHITE CRUCIBLES

1. *Graphite.*—The graphite crucibles used in the melting of brass, steel, and various alloys consist, essentially, of a mixture of graphite and clay, which is shaped, dried, and fired to a moderate temperature usually at or below 800° C. The properties of the graphite which render it so valuable in connection with this use are its refractoriness, which to a certain extent is imparted to the clay bond, its reducing effect, which prevents oxidation of the metal, and its high thermal conductivity, which makes possible rapid fusion of the charge. In addition, the smoothness of surface which it imparts to the crucible permits the clean pouring of the metal.

The function of the clay is that of a bonding material, which makes possible the shaping of the crucible and the cementing together of the graphite flakes. At the same time, it covers the particles, and thus protects them from oxidation. In order to be most effective in regard to this point, it is necessary that the clay

contract and become dense at as low a temperature as is consistent with the required refractoriness.

The manufacture of graphite crucibles consists in thoroughly grinding together and blending the graphite and clay, tempering with water in a suitable mixing machine till the mass has assumed the proper plastic consistency, shaping the crucibles by means of a pottery jolly, drying, and finally burning them.

It might be well to consider somewhat in detail the two essential raw materials, the graphite and the clay.

The modification of carbon known as graphite has been defined as that allotropic form which has a specific gravity of from 2.25 to 2.26. Certain chemical tests, such as that of Brodie, consisting in treating the graphite with fuming nitric acid and potassium chlorate, have been employed to differentiate it from other forms of carbon, though with variable success. Arsem² states that lampblack heated to a high temperature in the electric furnace, possessing none of the characteristic properties of graphite, yielded the yellow graphitic acid of Brodie's test, though the specific gravity was only 2.122.

As to the real nature of graphite we are still in the dark. It is crystalline, rhombohedral, and stable at the highest temperatures. Its great softness, flaky structure, and feeble metallic luster are characteristic. Its specific heat varies in the natural and artificial varieties and according to the purity of the materials. Values have been determined for Ceylon graphite of from 0.174 to 0.2019 and for blast-furnace graphite of from 0.166 to 0.1970. The specific heat increases with temperature and has been found to be 0.467 at 977° C. The coefficient of thermal conductivity of graphite (gram calories through 1 cm cube) is 0.0141, and hence five times that of burned clay. The linear coefficient of expansion is 0.0000786 at 40° C. The excellent electrical conductivity of graphite is well known, but is not of interest in this connection.

Graphite occurs in nature in several forms, more or less admixed with impurities. It occurs in the older crystalline rock, gneiss, schist, crystalline limestone, granite, and sometimes in carbonaceous shales and slates. Though often occurring in small flakes throughout schist, as in Alabama, it is also found in veinlike deposits of considerable thickness. Of this character are the occurrences in the Laurentian rocks of New York and Canada, the graphitic gneisses of the Eastern Alps, the granulites of Ceylon,

² Trans. Am. Electro-Chem. Soc.; 1911.

and the granites in Irkutsk, Siberia. Massive graphite occurs also in Sonora district, Mexico, at Borrowdale, Cumberland (England), Passau (Bavaria), Schwarzbach (Bohemia), in Portugal, on the island of Madagascar, and in the Province of Minas Geraes (Brazil). The Mexican graphite mines are considered the richest in the world. In point of quality for the manufacture of crucibles the Ceylon graphite is considered the best, and enormous quantities are exported from there to Europe and the United States. In this country the best-known deposit occurs at Ticonderoga, N. Y., but a large number of occurrences are to be met with in a number of States, as in Alabama, California, Pennsylvania, Georgia, North Carolina, New Hampshire, Rhode Island, Montana, and Virginia. Canada likewise possesses extensive graphite deposits. Large developments are under way at the present time in Alabama. In most American deposits the graphite occurs in small flakes interspersed in mica schist or similar rocks. The content of graphite scarcely ever exceeds 8 per cent, and it must be removed from the rocks by means of the usual methods of ore dressing. Of late oil flotation processes and electrostatic separation have been adopted successfully. As a rule, the domestic graphite is not as massive as the Ceylon product, consisting either of small flakes or, on the other hand, being more of a granular, amorphous character. The Ceylon graphite possesses to a marked degree a characteristic foliated structure combined with a low content of ash. Graphites differ widely in composition, and considerable variation is even observed in the Ceylon material. The purest grade of Ceylon graphite has been found to contain 98.87 per cent carbon, 0.90 per cent volatile matter, and 0.28 per cent ash. Frequently, however, shipments show a carbon content of 79.4 per cent and 15.5 per cent ash. In all graphites used for crucibles the ash content is of considerable importance, especially with reference to the amount of iron oxide present. If this constituent is too high it is apt to cause more rapid corrosion of the crucibles. Graphites have been examined in this laboratory which contain as high as 40 per cent of ash and 10 per cent of iron oxide. For the manufacture of graphite crucibles the Ceylon chip and flake graphite has been proven by years of practical experience to be exceedingly valuable. There is no reason, however, why Alabama graphite should not be used in admixture with the Ceylon product, or altogether for crucibles of the smaller dimensions, stoppers, and other accessories. The Ceylon graphite has an advantage in that it is of greater density,

which imparts to it greater resistance to oxidation. Its foliated structure and the possibility of sizing it to any desired series of grades, especially the coarser ones, cause the graphite-clay mixture to be more easily worked where large-sized objects are involved.

The fact that most domestic graphites are comparatively fine and of more uniform grain causes them to require more clay for bonding. To some extent this point is expressed by the volume occupied by unit weight of the different types of graphite. Thus, 100 grams of crushed Ceylon graphite, after thorough shaking, occupies a volume of 90.7 cc, Alabama graphite 152.0 cc, and Canadian graphite 119.6 cc, all three grades having been reduced to approximately the same size. This would tend to show that with the use of the maximum amount of American graphite bonded with clay, so as to be still workable, the carbon content would be smaller than when Ceylon graphite is employed. From this it follows that the ultimate density and thermal conductivity would be lower.

It is a fact that even with Ceylon graphite the sizing of the particles is of considerable importance, especially for crucibles used in the melting of steel, where it is desirable that the clay content be reduced to the minimum without impairing the density and strength of the product. This condition requires that the surface factor of the graphite be not too large, so that a relatively small amount of clay will suffice to cover and cement together the grains of graphite.

The computation of the surface factor may be illustrated by means of an example. A mechanical analysis was made of Ceylon graphite prepared by a commercial crucible plant and the dimensions of the particles determined by means of the micrometer microscope with the following result:

TABLE 3

Tyler sieve	Residue left on sieve, per cent by weight	Average dimensions of particles			Average surface area of particle	Surface factor = 1 ÷ average surface area
		Length	Breadth	Thick-Thickness		
		mm	mm	mm	mm ²	
On 20-mesh.....	30.30	2.06	0.92	0.272	5.4000	0.185
On 40-mesh.....	45.20	.96	.75	.111	1.8160	.550
On 80-mesh.....	18.34	.49	.35	.0457	.4190	2.386
On 100-mesh.....	2.19	.30	.214	.0252	.1543	6.480
Through 100-mesh.....	3.97	.12	.075	.02025	.258	38.76

Multiplying the percentages of the different sizes by their respective surface factors and adding, we obtain:

$$30.30 \times 0.185 + 45.20 \times 0.550 + 18.34 \times 2.386 + 2.19 \times 6.480 + 3.97 \times 38.76 = 88.06$$

as the surface factor of the graphite mixture. It will be noted that the surface factor increases very rapidly with the finer sizes. For this reason the amount of fine material must be regulated and kept as constant as possible for the same kind of work.

The purification of graphite, too high in ash content, by chemical means such as treatment with hot caustic-soda solution followed by washing with diluted acid, or with acid alone, has been carried on successfully in the preparation of graphite for the lead-pencil industry, but apparently is too expensive for crucible graphite. At the same time, such treatment requires fine grinding, which is not desirable for the purpose under discussion. It is interesting to note, however, that it has been possible to produce practically an ash-free product from graphite containing 11 per cent of mineral matter. The content of iron oxide may be reduced very largely by exposing the graphite to a current of chlorine gas at a temperature of approximately 600° C.

The simplest tests for the purity of graphite are the determination of its specific gravity and of the ash content.

The apparent specific gravity of American flake graphite was found to be 2.35, of Ceylon 2.36 to 2.43. There is, however, a variation in density according to the size of grain.

2. *Artificially Prepared Graphite and Carbon.*—Upon heating anthracite or coke to a high temperature in the electric furnace the carbon is converted into graphite. This transformation is practically complete and may result in as much as 99 per cent graphite. Owing to the great demand for artificial graphite for electrodes, lubricating, and other purposes, this material, from the standpoint of cost, is not available for crucible making. At the same time, its structure is not as desirable as that of the natural graphite, and its rate of oxidation under furnace conditions is appreciably greater. Graphite is formed also by segregation from cooling metal, as in the case of blast-furnace iron. Large quantities of scalelike graphite, known as "kish," are thus produced. The lamellæ of this type of graphite are exceedingly thin and fragile, and in incorporating a given weight of this material in clay much more of the latter and of water is required than when natural graphite is employed. Blast-furnace graphite, as a rule, contains a good deal of iron, which would make necessary purifi-

cation by means of an acid treatment. This type of graphite oxidizes more readily than natural graphite, and is also more readily absorbed by molten steel.

Sources of noncrystalline carbon are also coke, retort graphite formed in gas retorts, and the carbon resulting from the decomposition of hydrocarbons.

In European practice both coke and retort graphite have been admixed with the natural graphite for making crucibles. The practice is not desirable for steel melting, since the amorphous forms of carbon are more soluble in the molten metal than crystallized graphite, and hence cause too much cementation. Their more rapid rate of oxidation is likewise detrimental for this purpose.

Some of the Birmingham crucibles are said to be made up of 3 parts (by weight) of graphite, 2 of hard coke, 2 of Stourbridge clay, and 1 of ground sherds from old crucibles. Crucibles used in a Germany foundry have been made from a mixture consisting of 5 parts of ground coke, 4 of graphite, and 8 of Stourbridge clay and grog. If the necessity arose, it would be, of course, possible to use crucibles in which all the carbon is introduced in the form of retort carbon, coke, or electric-furnace graphite, even though the results were not as satisfactory as those obtained with the natural graphite.

It might be interesting to note that in melting an alloy of 68 per cent copper and 32 per cent zinc in a No. 60 crucible consisting of 50 per cent blast-furnace graphite, 6.75 per cent Maryland plastic bond clay, 12.5 per cent clay from Anna, Ill., 6.25 per cent Laclede-Christy bond clay, 12.5 per cent Kentucky ball clay, and 12.5 per cent siliceous bond clay from Lester, Ark., 25 melts were obtained. Considering the type of graphite and the high clay contents this is a very good showing.

In using electric furnace graphite an average life of 17 melts of the alloy given above were obtained from the two mixtures:

	Per cent	
Electric furnace graphite.....	55	60
Plastic clay from Laurel, Md.....	6	5
Plastic clay from Anna, Ill.....	10	10
Plastic clay, St. Louis, Mo.....	10	5
Ball clay, Mayfield, Ky.....	10	10
Plastic clay, Lester, Ark.....	9	10
	100	100

3. *Crucible Mixtures*.—As has been pointed out in previous paragraphs, the main requirements of a suitable crucible mixture are that it must possess satisfactory working qualities, good strength in the dried state, ability to withstand sudden temperature changes, good thermal conductivity, freedom from pinholes, sufficient mechanical strength to stand up under rough treatment with tongs, and slow oxidation of the graphite.

The clays most desirable for this purpose are those of the dense-burning type, which soften slightly at the heat of the brass furnace. The open-burning clays are not suitable for this purpose, though they may be used for the purpose of stiffening clays deficient in refractoriness. The amount of kaolin and other open-firing clays thus used must not ordinarily exceed 10 per cent. The clays to be considered here are those of the Klingenberg type; some of the English ball clays, such as that marketed as "Dorset;" the ball clays from Mayfield, Ky., and the Paris, Tenn., district; the bonding clay mixtures marketed at St. Louis, Mo.; the plastic bond clays from northern Mississippi, from near Portsmouth, Ohio, Laurel, Md., and Anna, Ill. The properties of these types of clays have already been discussed in detail in the preceding section. In every case those clays are to be preferred which vitrify close to 1150° C.

The compositions of graphite crucibles vary considerably with reference to whether they are to be used for brass or for steel melting. Some of the mixtures which have come to the knowledge of the writer are as follows: the first four being principally intended for melting brass and the last two for steel:

TABLE 4

	a	b	c	d	e	f
	Per cent	Per cent	Per cent	Per cent	Per cent	Per cent
Graphite.....	48	57.5	55	50	58	55
Bond clay.....	32	25.5	35	40	35	30
Kaolin, plastic.....	6	10.4	5			7
Sand.....				5	7	8
Crushed pot shell.....	14		5	5		
Potter's flint.....		6.6				

The addition of sand can be avoided by the use of a siliceous clay, like that from Arkansas (Lester), which makes possible a reduction of the clay content, if this is desirable, and yet the maintenance of good working quality. In making up crucibles with

55 per cent of chip and flake graphite good results have been obtained by the use of 8 per cent of sand and 37 per cent of a mixture of Maryland, Illinois, Missouri, and Kentucky clays, approximately in equal parts. Upon introducing Arkansas clay, which is very siliceous, no sand addition was found necessary, and the five clays were used in the proportion of 9 per cent each, thus making possible the use of more graphite or the partial substitution of flake for Ceylon graphite. The Mississippi clays have been found to be especially well suited for crucible making, and the large deposit available makes them a promising source of supply. As has been pointed out before, the blending of several clays is desirable for securing that combination of properties most satisfactory for the purpose. This makes it possible to arrive at a combination even more efficient than the use of the imported clay. At the same time, there would be less difficulty due to the unavoidable variations invariably met with in the mining of a single clay, since it is extremely improbable that all of the clays of the mixture should vary in the same direction at the same time. In making mixtures of any kind it is essential that the clays be blended intimately by mill grinding; otherwise the best results can not be obtained. The clay question should then resolve itself into the use of from two to four clays, which should constitute the standard batch and which should not be changed except for good reasons. Deficiency in refractoriness can be corrected by the use of kaolin; lack of density or insufficient vitrification by the use of a tight firing plastic clay, higher in fluxes; and inability to resist the pressure of the molten metal, as evidenced by the bulging of the crucible, by the addition of quartz.

For the purpose of securing data concerning the relative resistance to oxidation offered by mixtures composed of Ceylon graphite and clay in the proportion of 1:1, specimens were molded in the form of open cubical boxes measuring $3\frac{3}{4}$ inches outside and $2\frac{3}{8}$ inches inside, thus having walls $\frac{1}{8}$ inches thick. These were pressed in the plastic state, dried, inclosed in saggars containing coke, and fired in a kiln, to a temperature of 1125°C . The burnt specimens were then reheated in a muffle under decidedly oxidizing conditions at 1000°C . Every hour a specimen was withdrawn, cooled, and weighed. The loss of carbon due to oxidation was thus determined for each clay-graphite mixture. The results are compiled in Table 5.

TABLE 5

Bond clay	Porosity of clay at 1125° C	Per cent loss in weight, in terms of original weight, after oxidation at 1000° C continued for—						
		1 hour	2 hours	3 hours	5 hours	9 hours	17 hours	23 hours
	Per cent							
English ball clay.....	2.47	2.77	5.94	7.75	9.09	12.85	19.27	20.84
Southern Illinois clay.....	26.27	4.52	7.37	9.92	12.62	15.70	24.18	26.92
Tennessee ball clay.....	18.85	3.21	7.29	9.06	10.91	17.05	22.35	29.42
Klingenberg.....	3.80	3.77	8.63	10.30	11.80	17.67	25.72	30.20
Maryland.....	17.13	3.84	8.65	9.20	13.50	18.60	29.60	31.40
Kentucky.....	20.26	4.11	8.22	11.82	15.12	18.87	27.15	33.15
Missouri.....	17.85	5.19	9.19	11.50	13.96	19.44	31.02	34.25
Southern Ohio.....	19.15	5.18	11.35	11.05	15.00	22.80	31.75	34.60
Tennessee ball clay.....	19.03	4.00	9.65	12.80	15.20	24.30	30.40	36.70
Do.....	38.00	6.30	11.18	11.35	14.70	21.45	33.50	39.60

From these it follows that the Klingenberg clay is by no means the most protective material and is excelled in this respect by three other clays. On the other hand, the losses in weight are not as conclusive as might be desired, and seem to bear no close relation to the porosity as might be expected. The variation in loss due to oxidation does not fluctuate within wide limits. The outstanding fact is that low porosity, while certain to bring about some protective action, is not the sole factor involved.

An interesting fact, developed in some work done in this laboratory in the treatment of clays, might be promising from the commercial standpoint. In grinding soft lignite with water the latter assumed a dark-brown color, due to the suspension of very fine particles of carbonaceous matter. By using this liquid in place of the ordinary water, taking care to screen out all particles not passing the 120-mesh sieve, the bonding quality and toughness of the clay seems to be improved to an appreciable extent. This is somewhat analogous to the well-known process of Acheson, depending upon the use of tannic acid to improve the plasticity of clays, but does not have the bad effects of this reagent in the drying of the clay.

4. *Manufacture and Use of Crucibles.*—The preparation of the graphite consists usually in grinding it by means of a buhrstone mill or pan or disintegrator and sizing it by means of sieves. But a small amount of the dust is used, which is frequently utilized for nozzles, stoppers, and other articles. The sized mineral is usually stored in bins, from which it is weighed out in the proper proportions, together with the ground-clay mixture. The materials are then mixed together in the dry state, avoiding further grinding,

for which purpose a kneading machine may be employed. As soon as the dry mixing is completed water is added and the tempering continued until the soft plastic state has been attained and the whole mass is of uniform consistency throughout. The material is then allowed to cure or age for some time in the clay cellar. The crucibles are molded by means of the potters' jolly in plaster or metal molds lined with cloth. As regards to drying, the usual pottery practice is followed. The application of the modern humidity-drying methods, at least for the larger crucibles, should offer an opportunity for improvement, since uniformity of shrinkage is not always secured under the present conditions.

The firing of the crucibles is carried to a temperature but little above the temperature of complete dehydration of the clay, usually between 650 to 700° C. Even in muffle kilns some loss of graphite occurs on the surface of the crucibles through oxidation, as is evidenced by the white coating of clay. It would be presumptuous to say that we understand all the factors entering into the construction of the crucible body, nor do we understand clearly the various destructive agencies tending to shorten the life of crucibles.

It is obvious that laboratory work along these lines is difficult to carry on without having access to a crucible plant, as the question of workmanship enters vitally into the testing of the different mixtures. Much is yet to be learned. It is believed, however, that the future will show that the application of ceramic principles, so extensively applied in the production of porcelain and other clay products, are of service also in this connection. The American manufacturers of crucibles have been confronted by a serious situation, and they have done well under the circumstances, rendered especially difficult by the prevailing strenuous industrial conditions. Whether or not American crucible makers will return to the use of the Klingenberg clay remains to be seen.

It is quite apparent to the casual observer that the treatment to which graphite crucibles are subjected is often extraordinarily severe. In the first place it is doubtful whether the function of drying out the crucibles is properly understood. Graphite crucibles are not fired to a high initial temperature and hence retain a porous structure. In common with all other clay products not burned to vitrification the crucibles are hygroscopic; that is, they greedily absorb moisture from the atmosphere, which is more difficult to expel than we generally realize.

Low-fired clays differ widely as to their hygroscopic capacity and the temperature at which they release the moisture thus absorbed. At the same time, the expulsion of this moisture requires considerable time. Therefore, it is not sufficient simply to keep the crucibles in a warm place, but they should be finally maintained for at least several days at a higher temperature, say 150°C before being placed in the furnace. In Europe the crucibles on being taken from this kiln are sometimes covered with a waterproof coat, such as tar or pitch dissolved in turpentine.

The preheating of the crucible just before putting into the heat for the first time, likewise, is often too abrupt, and hence the temperature change to which they are subjected too violent. The ideal method of handling the fresh crucibles would be to place them in a special furnace kept heated by the waste gases of the melting furnace, where the temperature could be brought up uniformly to somewhat below red heat.

The conditions of heating are of great importance. It is evident that the intense heat of an oil burner will bring a large crucible far closer to the softening point than when it is exposed to the fire of a coke furnace. The larger the crucible and the higher the level of the liquid metal, the lower in temperature must be the failing point of the crucible, since at furnace temperatures even comparatively small loads tend to bring about deformation. Add to these factors the effects of unequal heating and rough handling, and it can readily be seen why the life of crucibles varies so widely.

II. GLASS WORKS REFRACTORIES

1. *Pot Mixtures*.—It has been assumed by American glass manufacturers that the refractories used by them, glass pots, tank blocks, floaters, boots, etc., for best results require the use of German clay, principally that obtained at Grossalmerode, the properties of which are discussed in the preceding section. The fact that this clay possesses good plasticity, safe drying qualities, low drying and low fire shrinkage, and at the same time, owing to its siliceous nature, resists the action of the commercial glasses very satisfactorily, has made it a standard raw material. The low temperatures employed in American pot arches have required the use of clays of low fire shrinkage, since evidently it is not admissible to permit the contraction taking place in the melting furnace to be too great, owing to the severe stresses to which the pots would be subjected.

Refractories for the glass industry are made, as a rule, from a mixture of calcined clay, consisting partly of crushed old pot material, carefully cleaned, and plastic bond clay. The proportion of calcined (grog) to plastic clay usually is between 1:1 to 3:2. In some glass plants no clay but the Grossalmerode material and pot shell was used; in others the plastic clay from Missouri was introduced, and, again, in some cases a smaller amount of raw flint clay was added. Some of these mixtures are as follows:

TABLE 6

Clay	a	b	c	d
	Per cent	Per cent	Per cent	Per cent
Grossalmerode clay, raw.....	47.0	20	24	25
Grossalmerode clay, burnt.....		10		
Missouri plastic clay, raw.....		20	16	20
Missouri clay, burnt.....	26.5		15	15
Flint clay, raw.....			15	10
Pot shell.....	26.5	50	30	30

These mixtures, taken as a whole, gave satisfactory results with the usual soda-lime glasses. It was taken for granted that the pots and tank blocks would have about so long a life, and it was also assumed, as a matter of course, that they would not last so long with lead or special glasses. The considerable, though uniform, solution of the refractories due to the presence of the siliceous German clay was not thought objectionable. The results were not so good when the proportion of the Grossalmerode clay was above the average, and especially in the case of the more corrosive glasses. In general, it was not realized that different refractories are required for different types of glasses, and unfortunately no special efforts were made, excepting by one or two large companies, to improve matters. With the outbreak of the war and the elimination of the German clay more or less confusion occurred, and the exclusive use of domestic clays was not always successful, for reasons which will be considered later. A search was made for substitutes, with the result that a number of new clays were brought on the market, and the mining operations of the well-known and reliable Missouri clays from the St. Louis district enlarged. Among the clays brought forward in this connection were the ball clays of Tennessee and Kentucky, already used to a large extent in the pottery and tile industries, the siliceous clay from Lester, Ark., the plastic fire clays from near Ports-

mouth, Ohio, and the clays from southern Illinois. The physical properties of these clays have already been discussed. The Arkansas clay was found to be very similar to that from Grossalmerode, but it required to be supplemented by a plastic, more aluminous clay, firing to a dense structure at a lower temperature, approximately 1250°C . For certain glasses satisfactory results have been obtained with the use of only the Missouri washed plastic clays in the raw and burned state, employing in addition about 10 per cent of calcined flint clay. In other cases, using some of the other clays mentioned, unsatisfactory results have been obtained, due principally to cracking of the pots around the bottom. The resistance of the American clays to corrosion has usually been very satisfactory and better than that of the German clay. The cracking must be ascribed merely to the greater firing shrinkage of the American clays.

2. *Fire shrinkage.*—The maximum temperatures of our pot arches are usually very low, to say nothing of their extreme irregularity. Rarely do they exceed 1000°C , which is entirely insufficient to cause more than a slight amount of heat contraction. The bulk of the shrinkage remains to be accomplished in the melting furnace under the most adverse conditions due to unequal heating and under the pressure of the glass charge.

The differences in contraction of the different clays are shown in the following table:

TABLE 7.—Contraction of Bond Clays

Clay	Drying shrinkage, in per cent of dry volume	Firing shrinkage, in per cent of volume in dried state, at temperatures of—				
		1050°C	1100°C	1200°C	1290°C	1400°C
Grossalmerode.....	20.57	4.14	7.84	8.55	10.70
St. Louis district.....	28.52	8.70	13.62	19.60	23.25	24.35
Tennessee ball clay.....	29.51	17.90	32.20	39.12	42.75	38.45
Kentucky ball clay.....	34.53	11.49	26.80	37.01	41.75	39.55
Southern Ohio, washed.....	40.61	7.08	14.50	20.20	26.02	25.41

These figures show the point brought out with unmistakable clearness. It will be noted that the fire shrinkage of the German clay is far less than that of the American bond clays. Assuming that the mean pot arch temperature is 1050°C , which is above the point usually reached, and that the mean furnace temperature is 1290°C , the Grossalmerode clay will contract about 7 per cent of the dry volume; the St. Louis clay, 14.55; the Tennessee ball

clay, 24.85; the Kentucky ball clay, 30.26; and the Ohio material, 18.94 per cent. Thus, allowing for a grog content of 50 per cent, the contraction in the furnace of a pot having a solid content of 10 cubic feet would vary from 0.75 to 1.5 cubic feet of displacement, a condition which taxes the strength of the body to the limit. The figures given show also one reason why the Missouri clays have been preferred for pot making, their fire shrinkage being the lowest of the American clays cited. It is evident, therefore, that the use of a siliceous clay like that from Arkansas with a fire shrinkage of only 1.6 per cent at 1290° C is greatly to be desired. Its exclusive use, however, is not desirable, as has been already stated, due to its too open structure, and its combination with a clay of the ball clay type should prove eminently satisfactory. The proper admixture can be approximately computed from the values given in the tables of Part I, both on the basis of shrinkage and desired density at the furnace temperature in question.

The large furnace shrinkage of American bond clays may be overcome by admixture with a siliceous clay or sand, by increasing the content of grog or by sizing,⁴ the latter to yield mixtures of minimum shrinkage (increasing the fines), and by the employment of higher pot-arch furnaces.

The use of siliceous clays probably offers the easiest remedy, since materials of this type are plentiful and are to be found in large quantities in New Jersey, as well as associated with many of the fire-clay deposits of Missouri, Kentucky, Tennessee, Ohio, Pennsylvania, and other States. It is not desirable to reduce the shrinkage of the clay or the pot body to its lowest possible value; but the fire contraction of the blended clay mixture (without grog) should be about 12 to 15 per cent, in terms of the dry volume, at 1300° C. It is obvious that exact limits can not be given to cover all cases. The introduction of more siliceous clay than is necessary to reduce the pot contraction to a value consistent with safe operation (freedom from fire cracks) is not desirable, since the rate of corrosion may become too great, especially in the case of flint glasses. Furthermore, the danger of fire checking due to the presence of too much free quartz is a distinct danger which is to be avoided. The exclusive use of Grossalmerode clay frequently has lead to this difficulty in the past, and from old records it has been learned that often such pots are considered "tender."

⁴Bureau of Standards Tech. Paper No. 104.

Chemical analysis is useful in checking the silica content of mixtures. It is evident that if in a clay mixture a silica content of 62 per cent is to be maintained and clays a and b contain 80 and 51 per cent silica, respectively, they must be blended in the proportion of 11:18.

For purposes of comparison an average analysis of Grossalmerode clay is given herewith:

	Per cent
Silica.....	73.08
Alumina.....	15.75
Titanium oxide.....	2.10
Ferric oxide.....	.62
Lime.....	.54
Magnesia.....	.33
Potash.....	.27
Soda.....	.16
Loss on ignition.....	7.11
Mineral composition:	
Clay substance.....	44.28
Quartz.....	53.03
Feldspar.....	2.69

3. *Porosity and Refractoriness*.—It is desirable that the porosity of the pot body be as low as possible when the glass charge is introduced, though it must be realized that this requirement is somewhat contradictory to the other condition, namely, that the fire shrinkage be low also. However, a compromise may be reached by employing with the siliceous clay a material burning dense at the furnace temperature. Thus the Grossalmerode clay has a porosity of 16.9 per cent at 1290° C, while the St. Louis district shows only 8.96 per cent. A combination of the two results in a value which is midway between these figures.

It is evident, again, that the Arkansas clay, having a porosity of 25.6 per cent at the above temperature, requires a larger amount of dense-burning clay to reach the desired degree of compactness. If to the siliceous material a clay could be added possessing a still lower porosity at the temperature mentioned, this would be a further improvement, providing, of course, that the refractoriness of the mixture was not lowered below the permissible boundary. Deficiency in refractoriness may be made up by the addition of kaolin or flint clay.

It is necessary to realize the fact that siliceous clays are more sensitive to the presence of fluxes than the more aluminous ones, and hence it is quite possible that by the admixture of a material of the first type with one of the second which is somewhat high in

fluxes, a complex eutectic may be formed, which causes the refractoriness to become too low.

Attention might be called also to the fact that careful drying of glass pots and tank blocks is essential, since not infrequently damage done by too rapid or irregular drying manifests itself when the pot has been placed in the melting furnace. The application of the humidity-drying systems promises to offer a solution of the difficulty in insuring safer drying conditions both as to temperature and steady drop in the vapor pressure of the moist air surrounding the objects to be dried.

4. *Preheating*.—It would seem most desirable also to depart from the old construction of the pot arches, which may be adequate for the smaller pots used formerly, but do not serve the purpose of preheating the large sizes commonly employed at the present time.

Temperature readings observed in arches show exceedingly wide variations between the top and bottom of pots. The bottom, subject to the most intense corrosive action of the batch, is usually underfired. The result is that the difference in shrinkage between the several parts brings about a severe stress, apt to lead to cracking, and at the same time the porous structure of the bottom leads to destructive corrosion.

It would seem desirable to abandon the present pot-arch construction entirely and to adopt either the down-draft or the up-draft firing so commonly used in the clay industries. It is likewise to be recommended that the firing be done from two sides, over bag walls, very similar to the arrangement of the rectangular down-draft kiln employed in brick burning. By the use of a perforated kiln bottom the heat and flames may be directed at will and can be caused to surround the bottom of the pots which are placed on blocks, thus insuring proper burning of this part. The use of either the down or up draft firing, provided ample draft is available, makes it possible to preheat the pots to a higher temperature, say 1200 to 1300° C. The result will be that the maximum amount of fire shrinkage will be accomplished where it should be and not left to be done in the melting furnace. The use of very siliceous clays then becomes no longer necessary, and more aluminous, denser materials may be employed which show better resistance to corrosion, especially in the melting of flint glasses.

Too little attention is given also to the heating up of pots and tank blocks. Much time is often consumed unnecessarily in the first heating while the dehydration and oxidation range,

500 to 800° C, is frequently passed too rapidly, resulting in permanent damage to the pots. Well considered heating schedules should be adopted, which result in a perfectly oxidized and sound structure. While this precaution is not of such great importance in the use of Grossalmerode clay, it becomes imperative when the denser American clays are used, since these nearly always contain more or less carbonaceous matter. The time required for passing through the range between 500 to 800° C may be determined with accuracy by firing with the pots a number of cubical blocks made of the same mixture, measuring say, 4 or 5 inches. Upon removing one of these specimens from time to time and breaking it the fracture should be of a light, uniform color, free from any gray or dark area in the center. The temperature must not be allowed to exceed 800° C until the dark core has disappeared and a block when drawn and split has the desired appearance. In this manner the rate of heating the arch may be established once and for all for a given pot composition. The time thus lost by holding within the temperature limits given may be regained by firing quite fast from this point to the maximum temperature, as no damage can be done. It is desirable, however, to hold the final temperature until the contents of the arch have been uniformly heated throughout. Such a firing schedule need not require more time than is being consumed by the old practice.

It is true that in using down-draft arches a stronger draft will be required, but a stack 50 feet high should be ample for the purpose. The regulation of the draft by means of a flue damper is necessary and will result in saving of fuel.

It is not improbable that the pot arch of the future will be of the continuous-tunnel type, in which the pots are placed and fired on cars similar to the kiln already employed in some of the clay industries.

What has been said of glass pots applies in general to tank blocks. In these the importance of a sound molding structure and of uniform firing to a fairly dense structure is even greater, owing to the heavy cost involved in cooling down a tank furnace. It is very probable that in the future the hand molding of blocks will be replaced by pressing on a large auger machine or piston press to prevent the structural irregularities so difficult to avoid in hand work. It is necessary also that more attention be paid to the thorough oxidation and more complete burning of the blocks.

III. SPECIAL POTS FOR THE MELTING OF OPTICAL GLASS

1. *Semiporcelain and porcelain pots.*—It was realized at the very initiation of the work on optical glass, begun in the Pittsburgh laboratory of the Bureau of Standards about five years ago, that the production of suitable pots plays an important part in the manufacture of this type of glass. It is evident that the pot material must resist corrosion by the glasses, some of which are very active in this respect. The solution of the clay body in the glass causes serious difficulty through the production of striæ due to disturbance of the homogeneity, resulting in threads or strings which are stirred into the molten mass. It should be stated here, however, that solution of the pot is not the only cause of striæ, but that they may be due to lack of homogeneity in the glass itself. Again, it has been observed that the constituent of the pot body first dissolved by the glass is iron oxide. The coloring power of iron, especially with the heavy flint and barium glasses, is very intense, so that very small quantities suffice to impart to the melt a very decided yellow or green shade. This coloration is injurious not only for optical reasons with reference to photographic purposes, but it is a powerful factor in cutting down the light transmission. Since the use of decolorizers is out of the question in optical glass, owing to the high absorption of light caused by them, it is obvious that the content of iron oxide must be kept down by the use of practically pure reagents and by the use of pots as low in this constituent as possible. It will be readily seen that by the use of the ordinary type of pot the amount of iron brought into the solution might easily be several times that of the original iron content of the entire glass batch. The use of even the purest reagents would thus be of no avail.

It would appear that pots used for this purpose should be resistant to corrosion by the molten glass, yet sufficiently refractory to withstand the high temperature of the furnace, which may approach 1475°C , and the hydrostatic pressure of the liquid charge, and should be as low in iron oxide as possible. Since the pots are used but once, the thickness of the bottom and walls may be cut down to the minimum. Owing to the high value of the glass, the cost of the pot, within obvious limits, is not a serious consideration.

The first pot mixture used in this laboratory, when operations were begun on a larger scale, was as follows:

	Per cent
Laclede-Christy bond clay, 69-B.....	6
Tennessee ball clay.....	5
Bond clay from Anna, Ill.....	7
Kentucky ball clay.....	5
"Highlands" fire clay, St. Louis.....	5
North Carolina or Delaware kaolin.....	12
Calcined "Highlands" clay, 10-mesh.....	20
Calcined kaolin, through 16-mesh.....	40
	<hr/> 100

In using this mixture it is necessary to calcine the kaolin to a temperature of not less than the softening point of cone 14. This, of course, increased the cost of the pots. Later, the calcined kaolin was replaced by a mixture of 80 per cent kaolin (North Carolina, Florida, and Georgia in equal parts), 10 per cent of flint, and 10 per cent of feldspar, fired also to cone 14. This gave a sharper and less friable grog. Both compositions gave excellent results with reference to the standing-up qualities and the resistance of the pots to corrosion. Still, the iron content of the mixture was somewhat too high, and it was thought desirable to work out a composition akin to that of a hard porcelain. After some experiments the following composition was arrived at:

	Per cent
Calcine.....	43
Kaolin.....	25
Plastic bond clays.....	25
Feldspar.....	7
	<hr/> 100

Here, the calcine consisted of the kaolin, feldspar, and flint mixture mentioned above. It is evident that in blending such a number of materials great care is necessary to secure thorough dry mixing and pugging. These pots likewise gave very satisfactory results.

The question of procuring the calcine in larger quantities was found to be an annoying one, and a cheaper source of grog was sought. This was found in the waste bisque of white-ware potteries, which is obtainable at a reasonable price and in sufficiently large quantities. This type of body corresponds to the general composition of 35 per cent kaolin, 15 per cent ball clay, 14 per cent feldspar, and 36 per cent flint. The white-granite bisque softens at about cone 30 and possesses, on account of the high flint content, excellent standing-up qualities under conditions of

pressure and at high temperatures. It is evident that porcelain bisque, whether tableware, electrical porcelain, or floor tile, would not answer for this purpose, owing to the low refractoriness. There would be no objection, of course, to the use of this kind of material in replacing the feldspar introduced, the proportions of white-ware bisque and porcelain bisque introduced being such as to maintain the desired refractoriness. In employing white-ware bisque it should be obtained in as clean a condition as possible, and care should be taken not to produce too large a percentage of fines (finer than 80-mesh) in grinding. If this grog should become too fine, it might cause serious cracking of the pots during cooling, probably at a temperature of about 625°C , when the glass is still in a semifluid condition. This defect is due to vitrification, facilitated by the presence of the fine particles of grog and the resulting homogeneous porcelain structure. In satisfactory pots the grains of grog should still retain their identity as shown by their outlines.

For some time both white-ware bisque and old pot shell (from porcelain-type pots) have been used, and the composition of the pot batch is as follows:

	Per cent
White-ware bisque, through 10-mesh.....	35
Pot shell, through 10-mesh.....	10
Feldspar.....	3
Flint.....	4
Tennessee ball clay, No. 5.....	15
Kentucky bond clay, No. 4.....	5
Kaolin.....	28
	<hr/> 100

The ground and screened grog and other components of the body batch are weighed, mixed, and then tempered in a wet pan. It is desirable in tempering that the mullers be raised about one-fourth inch off the bottom of the pan, so that the grinding action is reduced to the minimum. The clay is then passed through a vertical pug mill and stored as long as possible. The body should be aged at least a month. The treading of the plastic body has been discontinued. The pots are built up by hand in the usual manner, and both the open and covered types are made. The pot used in this laboratory is 34 inches in diameter (outside), 27 inches high, and has a bottom 4 inches thick. The wall tapers from $2\frac{1}{2}$ inches (top) to $3\frac{1}{2}$ inches (bottom). The weight of each pot is about 550 pounds. After drying for about four weeks the pots are ready for the furnace.

2. *The Casting of Pots.*—One or two pots each week are also being made by the casting process. The composition of this body is as follows:

	Per cent
White-ware bisque.....	48
Plastic bond clay.....	22
Kaolin.....	23.5
Feldspar.....	6.5
	<hr/> 100

The slip used carries 80 per cent of solids, and hence 20 per cent of water. A mixture of sodium silicate and sodium carbonate in the proportion of 4:3 is used as the electrolyte and the amount added, in terms of the dry weight of the body, is 0.20 per cent as the anhydrous salts. The arrangement of the mold, as shown in the illustration, Fig. 24, needs no detailed description. It is, of course, necessary to hold the core firmly in position by means of crossbeams and tie-rods, as the upward hydrostatic pressure of the slip is considerable. The casting, as now practiced, is through three funnels arranged symmetrically around the circumference of the mold. The liquid in the funnels is replenished as the level is lowered. During the last stage of the casting the settling is very slow, so that the funnels may be filled and the process allowed to go on without close supervision. Absorption of the liquid ceases after about 16 hours, and the core may then be removed. The outer mold may be removed after 24 hours. Suitable hoists are necessary for the handling of the mold parts and the pots.

The process of preparation of the slip is very simple, consisting in introducing the weighed, ground body constituents into a double blunger, together with the required amount of water in which the electrolytes have been dissolved. When the desired consistency has been attained, the slip is allowed to run into a large bucket, which is conveyed to the mold, hoisted, and the slip discharged into the funnels. No difficulty has been experienced in drying the cast pots in less than four weeks. They have given very good satisfaction in the glass furnaces and, if anything, are superior to the handmade ones, especially on account of the fact that they have thinner walls, the thickness varying from 2 to 3 inches. For this reason less time is required in the heating up period.

In the use of porcelain-type pots it is important to raise the temperature of the furnace to not less than 1400° C, before the charge is introduced, in order that the body may become vitri-

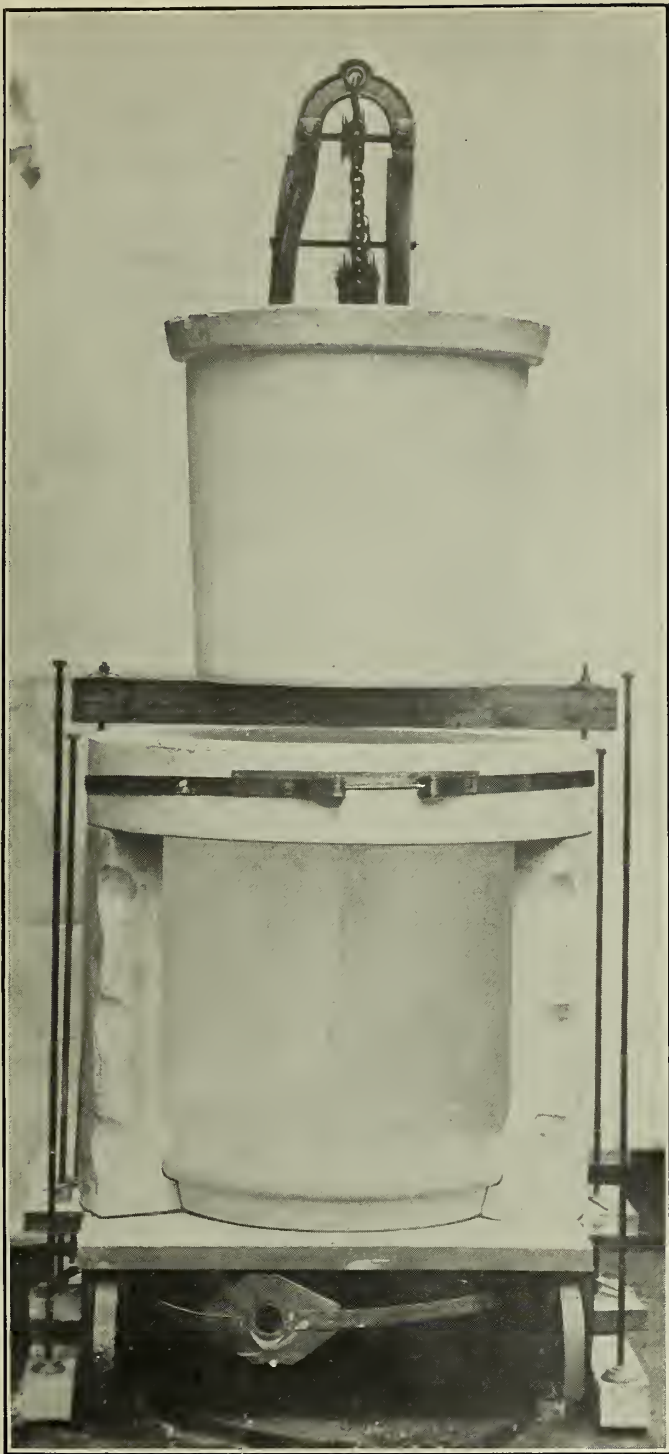


FIG. 24.—Mold used for the casting of glass pots, with core removed

fied. The temperature may then be lowered, and the glass batch introduced into the pot. Unless this is done the benefits of the porcelain structure are lost, and the pot may corrode as much or more than one of the ordinary type.

The same body composition is also used in the casting of the stirring-rod parts, which are immersed in the glass during the mixing stage of the melt.

IV. SUMMARY

The physical properties of three typical German clays formerly imported in large quantities have been described in detail and on the basis of constants, which make possible accurate comparison and evaluation of American materials. Similarly, the physical characteristics of 23 American and 2 English bond clays have been determined. Of these several approach the Klingenberg and Grossalmerode clays quite closely. Others, by suitable blending, can be made to equal or excel the European clays.

For crucible making the best clays should show a pore-shrinkage water ratio of not more than 1:1; a modulus of rupture for a clay-sand mixture of 1:1 of about 325 pounds per square inch; a vitrification point of 1150° C, or lower; no marked evidence of overfiring at 1,400°, C; and a softening point corresponding to Orton cone 31, or above. For glass pots the best materials should show a pore-shrinkage water ratio of not more than 1:1; a modulus of rupture, when mixed with equal weights of sand, of not less than 250 pounds per square inch; a vitrification temperature of approximately 1,275°, C; an overfiring temperature not below 1,425°, C; and a softening point equivalent to Orton cone 29, or above.

The value of graphite for crucible making is expressed by the factors of density, surface factor, and ash content. Artificial graphite and coke might possibly be used, but are subject to certain limitations.

The usefulness of the Grossalmerode clay for glasshouse refractories is due principally to its low fire shrinkage. Its ability to dry without checking or cracking even under adverse conditions is another desirable feature. While its resistance to corrosion by the melt is sufficient for glasses of the soda-lime type, it does not stand up well in contact with flint glass. The rigidity of this siliceous clay at furnace temperatures—that is, its ability to resist pressure without deformation—is another point in its favor. On the other hand, it is apt to be somewhat tender as

regards mechanical manipulation in the furnace and shows a tendency to spall under sudden temperature changes.

Conversely, most American bond clays dry somewhat more difficultly than the German clay and show a greater drying and firing shrinkage. When properly prefired, on the other hand, they resist the corrosion of glass more satisfactorily. Siliceous clays are found in the United States which duplicate the Grossalmerode clay. It is not desirable to go as high as the silica content of the imported material in order that the density of structure may be not impaired too greatly. The disadvantage of the greater fire shrinkage in the furnace may be overcome, first, by the addition of a very siliceous clay in the raw state to the more aluminous bond clays; second, by the introduction of some calcined siliceous clay (grog), passing an 18-mesh sieve, in the pot batch; and, third, by prefiring the pots or blocks to a higher temperature than is customary, thus bringing about the bulk of the shrinkage before the objects are placed in the melting furnace. Large deposits of highly siliceous clays are available in the United States.

It is urged that the construction of pot arches be changed to a type making possible more uniform temperature distribution, as well as higher temperatures. The down or up draft kilns with perforated bottoms, used extensively in the clay industries, are recommended. The rate of heating the pot arches should conform to the critical temperature ranges applying to clay, viz, the expulsion of the hygroscopic and of the combined water and the oxidation of carbon. Halts should be made within these ranges until the changes involved are completed. Between and beyond the critical temperatures the heating may be more rapid than prescribed by the present practice.

For the melting of optical glass the use of semiporcelain or porcelain pots is recommended. Compositions are given for mixtures of this type. The use of waste white-ware pottery bisque is suggested as a source of grog. Finally, the procedure of casting glass pots as practiced at the Pittsburgh laboratory of the Bureau of Standards is described.

The writer desires to express his appreciation of the laborious work done by G. A. Loomis in the careful testing of the clays which have been described, and the cooperation of F. H. Riddle, J. W. Wright, and W. W. McDanel.

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